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STUDIES ON SOILS, PART I: THE UPWARD MOVEMENT OF WATER AND SALT SOLUTIONS IN THE BLACK COTTON SOIL*

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Received February 16, 1942

1. Introduction

In the Deccan a dry surface crust containing only hygroscopic moisture is formed within a few weeks after the cessation of wet weather. This surface layer loses moisture by day and reabsorbs it from the atmosphere at night, thus tending to remain in equilibrium with the air layers above it and setting a limit to the continuous loss of moisture from the soil layers below. This protecting action makes dry farming possible in these areas where the soil rests on a hard layer of rock or murrum out of reach of any sub-soil water, the main source of moisture being the few post-monsoon showers. The Agricultural Meteorology Section at Poona has published the results of a detailed investigation of the above problem in a series of papers from 1934 onwards.[1–11]

A few years ago we took up the investigation of another equally important problem, *viz.*, the upward movement of moisture and salts through a soil layer resting on a water table. Such conditions exist in many parts of India where the water table is only a few feet below the soil surface. The problems connected with artificial sub-soil irrigation are also similar. In a recent publication[12] we reported the results of experiments on the effect of varying the distance between the soil surface and the water table on the rate of evaporation. Later, Mallik[13] discussed the movements of salts in columns of soil, originally uniform as regards their salt content, after a few months of ascent of moisture through the soil and continuous evaporation from the top of the soil surface. In the above papers it was shown that (1) the rate of evaporation after ascent of moisture through columns of Poona black cotton soil and normal alluvial and "bari" (alkali) soils of the Punjab decreases rapidly as the distance between the soil surface and the water table

* Read before the Annual Meeting of the Indian Academy of Sciences at Nagpur on the 25th December 1941.

is increased and (2) that the salts in the soil move with the ascending moisture and concentrate at the top of the soil columns. In these experiments the measurements were made with the help of soil evaporimeters. The soil columns 5″ in diameter and of different depths were packed in brass cylinders with perforated bottom and dipped in a lower vessel containing water up to a standard level.

To examine the ascent of water and the associated phenomena in greater detail *visually*, a series of experiments were undertaken recently at the Central Agricultural Meteorological Observatory, using glass tubes filled with the soil specimens. In Part I of this series we shall describe some of the preliminary experiments on the ascent of water and dilute salt solutions through the soil. In Part II the results of a microscopic examination of the swelling action of a number of salt solutions on the black cotton soil and some further experiments on the movement of these solutions through the soil will be discussed. Part III will contain a discussion of some physical and chemical aspects of these phenomena in the light of a number of detailed experiments on the effect of concentration of the salt dissolved in water on the rate of movement of the solution through the soil.

2. *The Movement of Water through the Soil in Relation to the Packing of the Soil*

In experiments of this nature it is very important to know the influence of packing on the rate of movement of water through the soil. Mr. P. S. Sreenivasan, working in our laboratory, is investigating the problem of the velocity of the movement of moisture through soils under (*a*) the combined action of gravity and capillarity (downward flow), (*b*) the opposing influences of gravity and capillarity (upward flow) and (*c*) the influence of capillarity alone (horizontal flow). A detailed discussion of his results will be presented in a separate communication. We may mention here that in one of his experiments on the horizontal flow of water through a soil column the length of the wetted column of soil (in a glass tube 1·3 cm. in diameter) in a given time was found to decrease with the length of the tube occupied by the same quantity of soil.

For *minimum* packing, the *maximum* volume occupied by four ounces (113·6 gr.) of the soil was 99·3 c.c. and for *maximum* possible packing the minimum volume of the same quantity of soil was 84·3 c.c. Thus 15·0 c.c. was the maximum possible change in the volume of the soil due to packing. The lengths of the wetted column of soil after 24 hours in tubes with soil of different degrees of packing are given below:—

Degree of packing	Length of the soil column wetted in 24 hours
	cm.
0% (minimum packing) ..	81·4
15%	72·3
33%	63·4
50%	55·3
66%	49·3
80%	35·7
100% (maximum packing) ..	26·6

It is clear that the length of the soil column wetted in 24 hours for minimum packing is nearly three times that for maximum packing. The importance of packing in our experiments is brought out very strikingly by these results. To ensure the uniformity of packing in a series of experiments, as far as possible, the following procedure was adopted for Poona soil.

The necessary amount of air-dry soil, passed through a 0·5 mm. sieve, is poured into the glass tube. The bottom of the tube is closed before-hand by a piece of muslin stretched across the open end, folded up and tied suitably at the sides. The glass tube with the soil is then held vertically and dropped on the table four times from a height of 3 inches.

To study the variability of packing in the case of Poona soil, 110 gr. of the soil were poured into the same glass tube and the length of tube occupied by the soil after attaining the standard packing was measured repeatedly (20 times). The mean length and the standard deviation were 77·7 cm. and 0·23 cm., respectively, indicating a coefficient of variability of only 0·3%.

3. Ascent of Water in 12 *Glass Tubes filled with Soil and Packed as described in the Preceding Section*

To study the variability in the rate of ascent of moisture, twelve glass tubes of internal diameter 1·3 cm. (the size used in all the experiments discussed in this paper) were packed similarly with soil according to the method described above. The lower ends of these tubes were inserted in water contained in suitable bottles. The heights of the wetted column in the different tubes were recorded at short time intervals at the beginning when the rate of ascent is very rapid and at longer intervals later on. Table I gives the mean height of the wet column, its standard deviation as well as the coefficient of variability, (*i.e.*, $\frac{\text{standard deviation}}{\text{mean}} \times 100$)

Fig. 1 gives the mean height of the wet column at different times after the commencement of the above experiment. The curve is exponential,

TABLE I

Time after commencement of experiment	Mean height of wet column in cm.	Standard deviation	Coefficient of variability %
5 mts. ..	7·0	1·38	20
25 mts. ..	8·9	1·48	17
40 mts. ..	12·2	1·64	13
1 hr. 10 mts. ..	16·2	1·85	11
2 hrs. 10 mts. ..	21·5	1·75	8
3 hrs. 10 mts. ..	25·0	1·72	7
4 hrs. 40 mts. ..	28·8	1·43	5
6 hrs. 40 mts. ..	32·6	1·19	4
9 hrs. 40 mts. ..	36·6	1·04	3
11 hrs. 40 mts. ..	38·5	0·98	3
21 hrs. 40 mts. ..	44·7	1·09	2
45 hrs. 40 mts. ..	52·6	1·14	2
70 hrs. 25 mts. ..	57·0	1·28	2
93 hrs. 40 mts. ..	60·3	1·36	2

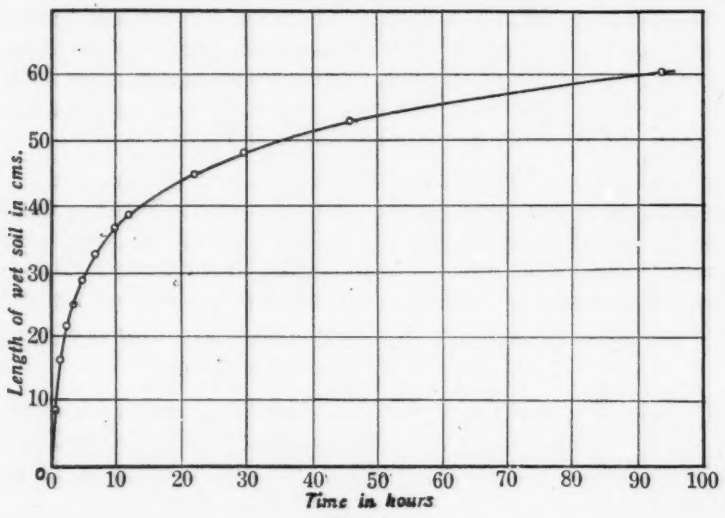

FIG. 1

with a rapid rise in the beginning and a gradual flattening later. The coefficient of variability is of the order of 20% to start with but decreases very rapidly to about 10% after an hour and to 5% in 5 hours. The variability is only 2% towards the end of the experiment. The standard deviations are more or less of the same order of magnitude.

If four replications are used the percentage variability in the later stages will be of the order of 4%. As will be clear later on, the variations due to

specific causes will be much higher than 4% so that four replications will be sufficient for estimating the variability due to random causes. With a few exceptions, four replications were generally used.

4. Rate of Ascent of Moisture in Poona Soil in Sand and in Mixtures of the Two in Different Proportions

Permeability and pore space are important factors in controlling the movement of water through the soil. It is common experience that in a sandy medium the rate of movement is more rapid at the beginning although the maximum ascent will be larger ultimately in a clayey medium. To illustrate this the results obtained in Poona soil, sand and mixtures of the two in varying proportions may be cited.

The material used in this experiment was as follows:—

(i)	100 %	Poona soil
(ii)	85·7%	Poona soil the rest being sand
(iii)	71·4%	,, ,, ,, ,, ,, ,,
(iv)	57·1%	,, ,, ,, ,, ,, ,,
(v)	42·9%	,, ,, ,, ,, ,, ,,
(vi)	28·6%	,, ,, ,, ,, ,, ,,
(vii)	14·3%	,, ,, ,, ,, ,, ,,
(viii)	0 %	,, ,, ,, ,, ,, 100% sand

The above samples were filled in eight sets of two tubes each, in all 16 tubes, according to the standard method described at the end of Section 2. Only water was used as the ascending fluid. Table II gives the mean heights of the wet columns of soil after various time intervals up to 30 hours.

TABLE II

Ascent of Moisture in cm. in Poona Soil, Sand and in Mixtures of the Two in Different Proportions

Time after commencement of experiment	Percentage of Poona soil							
	100% Poona soil	85·7%	71·4%	57·1%	42·9%	28·6%	14·3%	0%
10 mts. ..	2·7	6·8	8·3	11·7	12·5	**15·3**	13·3	6·3
20 mts. ..	5·8	10·0	11·9	16·1	16·9	**19·5**	15·9	6·7
30 mts. ..	8·0	12·9	14·8	19·4	20·0	**22·3**	16·9	6·8
45 mts. ..	10·7	15·7	17·6	22·3	23·4	**25·3**	18·5	6·9
1 hr. 00 mt. ..	12·8	18·1	19·9	24·2	25·8	**26·8**	19·7	6·9
2 hrs. 00 mt. ..	18·4	24·4	25·9	30·4	**31·1**	30·6	21·8	7·0
3 hrs. 00 mt. ..	21·7	28·6	29·6	33·9	**34·3**	32·7	23·1	7·2
5 hrs. 30 mts. ..	27·2	35·5	35·5	**38·8**	39·0	35·3	24·3	7·3
8 hrs. 00 mt. ..	32·4	39·2	38·6	**41·4**	41·2	36·4	24·9	7·6
12 hrs. 30 mts. ..	37·5	43·4	41·9	**43·5**	**43·8**	37·9	27·3	8·0
24 hrs. 00 mt. ..	43·4	**51·3**	47·5	48·3	47·7	40·7	28·9	8·5
30 hrs. 00 mt. ..	45·2	**53·3**	49·6	49·6	48·5	41·8	29·2	8·6

It may be seen that:—

(i) the movement of moisture is initially more rapid in pure sand than in pure Poona soil; while the ascent continues uniformly in the Poona soil, it slows down in sand after the first 10 minutes.

(ii) in the mixtures of Poona soil and sand, the ascent is more rapid than in the pure samples, the rate to start with increasing with decrease in the percentage of Poona soil down to 28·6% and decreasing for smaller values. This continues during the first hour after the commencement of the experiment. Later on, the maximum rate of ascent shifts gradually towards the mixtures containing larger and larger proportions of Poona soil. If the experiment had been continued sufficiently long it would have been found that ultimately the height of the wet column is maximum in the Poona soil. These results are indeed very interesting and further experiments on these lines are being arranged with other typical soils of the country.

5. Rate of Ascent of Water and Dilute Solutions of Some Salts

Before starting replicated experiments with solutions of salts, etc., a preliminary experiment was done with 2% solutions of a number of available salts using only one tube filled with Poona soil in each case. The heights up to which water and the solutions ascended in 26 hours are given below:—

TABLE III

Nature of ascending fluid	Height of wet column in cm. at the end of 26 hours	Nature of ascending fluid	Height of wet column in cm. at the end of 26 hours
	cm.		cm.
Water	37·8	Sodium borate	42·3
Lithium carbonate	**0·0**	Sodium phosphate	35·6
Sodium chloride	43·8	Sodium carbonate	**1·8**
Sodium sulphate	35·2	Potassium carbonate	37·8
Sodium nitrate	43·0	Potassium hydroxide	44·7
Sodium hydroxide	40·8	Potassium chlorate	48·5

It is obvious that while many compounds do not affect the rate of ascent materially *there are a few very conspicuous instances like the lithium and sodium carbonate* in which the flow of water is almost completely impeded.

Effect of Lithium Carbonate, Sodium Carbonate, and Potassium Carbonate Solutions.—We may now examine in more detail the effect of equivalent solutions of lithium carbonate (0·35%), sodium carbonate (0·50%), potassium carbonate (0·72%) and water. The ascent of the above solutions and water

in Poona soil under standard packing was measured with four replications. Table IV gives the mean heights of the wet columns and the coefficients of variability (C.V.).

TABLE IV

Time	Lithium carbonate 0·35%		Sodium carbonate 0·50%		Potassium carbonate 0·72%		Water	
	h. in cm.	C.V. %	h. in cm.	C.V. %	h. in cm.	C.V. %	h. in cm.	C.V. %
30 mts.	0·7	73	1·2	21	4·5	19	3·8	18
1 hr. 15 mts.	1·1	56	1·5	17	6·8	13	7·0	14
2 hrs. ..	1·2	50	1·7	16	7·6	13	8·9	11
4 hrs. ..	1·7	39	2·2	19	8·6	14	13·7	8
7 hrs. ..	2·1	37	2·4	17	9·6	15	18·8	7
14 hrs. ..	2·6	33	3·0	12	11·1	15	26·9	5
24 hrs. ..	2·9	33	3·2	15	12·9	15	35·5	4
32 hrs. ..	3·0	33	3·5	14	14·3	16	40·0	6
48 hrs. ..	3·4	25	3·7	13	16·3	16	47·9	3
72 hrs. ..	3·8	22	4·1	14	19·1	15	56·1	2

Lithium carbonate affects the rise of water more than sodium carbonate. The rise of the potassium carbonate solution is much more rapid, but not quite as fast as that of water. The regular sequence in the effect of the salts of the different metals of the same group may be noticed, but we shall refer to this point at greater length in the second part of this paper.

Effect of Different Concentrations of Sodium Carbonate.—Next we shall consider an experiment with four replications in which the effect of different concentrations of sodium carbonate was studied. The concentrations used were 1·000%, 0·500%, 0·125% and zero per cent. (water). Table V gives

TABLE V

Rise of Sodium Carbonate Solutions of Different Strengths

Time	1·000%		0·500%		0·250%		0·125%		0%	
	Mean	C.V.%	Mean	C.V.%	Mean	C.V.%	Mean	C.V.%	Mean	C.V.%
	cm.									
10 mts. ..	0·8	25	0·7	27	1·1	9	1·3	18	1·1	27
20 mts. ..	1·5	9	1·4	7	2·0	9	2·9	11	2·7	20
30 mts. ..	1·8	12	1·5	7	2·3	7	3·9	7	3·6	18
45 mts. ..	1·9	11	1·8	8	2·6	10	5·0	3	5·1	17
1 hr. ..	2·0	7	2·0	0	2·7	8	5·5	3	6·0	18
2 hrs.	2·3	6	2·5	4	3·4	10	6·9	2	9·3	16
3 hrs.	2·5	4	2·7	5	3·7	9	7·7	3	11·7	14
4 hrs.	2·5	4	2·9	6	4·0	9	8·3	2	13·8	12
6 hrs.	2·5	4	3·1	6	4·5	9	9·2	3	16·7	10
8 hrs.	2·7	4	3·2	4	4·7	10	9·9	3	19·8	8
14 hrs.	3·0	3	3·9	4	5·3	8	11·2	3	26·1	6
25 hrs.	3·3	3	4·3	5	5·9	8	12·7	3	34·3	6
32 hrs.	3·3	4	4·5	4	6·3	9	13·5	4	38·4	6
48 hrs. 45 mts. ..	3·7	5	4·7	4	6·7	7	14·4	4	45·7	8

the mean ascent of the solutions and water in Poona soil and the co-efficients of variability (C.V.). The mean heights reached by the different solutions and water at different time intervals are shown by the series of curves in Fig. 2. These curves show very clearly the rapid decrease in the rise of the solutions

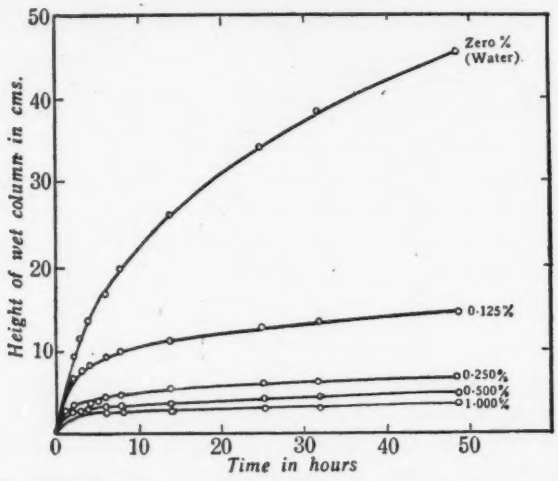

FIG. 2. Rise of differeut concentrations of sodium carbonate solutions in Poona soil

in soil on changing from water to 0·125% and ·250%. The effect of increasing the concentration is to decrease the ascent of moisture further; but most of the variation takes place from zero to 0·125%.*

5. *Conclusion*

In the present paper a simple laboratory method of studying the ascent of moisture and aqueous solutions through the soil is described. The effect of packing on the rate of upward movement has been discussed; it is shown that at *maximum* packing the rate of movement is only one third of that at *minimum* packing. To estimate error, four replications of each treatment are generally used. The influence of various percentages of sand mixed with the black cotton soil in increasing the permeability and rate of upward movement of moisture is discussed. The influence of small quantities of

* *N.B.*—The effect of concentration of the solute on the rate of ascent of solutions through the soil is under more detailed investigation, with a number of compounds. It is found that very dilute solutions actually cause an *increase* in the rate of ascent and that the decrease in ascent comes into effect only when the concentration is increased beyond a critical value, which varies with the substance. The critical concentration in the case of sodium carbonate is found to be about 0·02%. The results will be discussed in Part III of this series.

certain compounds is examined and it is shown, for example, that a small quantity of lithium or sodium carbonate reduces the rise of water very conspicuously. Lithium carbonate is more efficient in this respect than sodium carbonate. Other salts like nitrate, chloride, sulphate, borate, phosphate of sodium or sodium hydroxide do not affect the rise of moisture like the carbonate.

As compared to lithium and sodium carbonates, potassium carbonate shows little effect on the movement of water through the soil. The effect of concentration has also been referred to in the case of sodium carbonate.

These experiments are being repeated with a series of other compounds and different typical soils and the results obtained will be discussed later on. The importance of these phenomena in irrigation practice and in agriculture may be emphasized.

Experiments have been made to elucidate further the actual effect of some salts in checking the rise and movement of water. Microchemical methods have been freely used in this connection. A discussion of this work is being given in Part II of this series.

In conclusion, our best thanks are due to the Director-General of Observatories for providing the necessary facilities for this investigation.

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CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part III. A Study of the Characteristic Crystalline Components of Certain Citrus Fruits (Oranges of the Circars)

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Oranges of the Northern Circars belong to the three important species of the citrus, (1) *C. aurantium*, (2) *C. medica* and (3) *C. decumana*. They can be characterised in general as the sweet, sour and bitter groups respectively and this is supported by the following analytical results relating to the most important varieties of these three species.

Table I

Composition of juice %	*C. aurantium* or sweet group		*C. medica* or sour group		*C. decumana* or bitter group	
	Batavias	*Kamalas*	*Naranja*	*Dabba*	*Shaddock*	*Matheepala*
Acids as citric acid ..	0·85	0·63	3·0	7·4	1·0	6·9
Reducing sugars ..	3·1	3·5	3·8	1·5	3·4	2·3
Sucrose	4·6	3·8	1·2	..	3·7	..
Total sugars	7·7	7·3	5·0	1·5	7·1	2·3
Total solids	10·2	10·1	9·8	9·3	9·6	9·3
Mineral matter ..	0·54	0·52	0·47	0·43	0·48	0·45
Vitamin C (mg. per 100 g. of the juice)	48	43	44	28	38	36
Juice, % fruit	46	48	46	40	39	37

The fruits belonging to the species *aurantium* with sweet juice have high sugar content, the amount of acid being small. The position is just the opposite in the case of the species *medica*. In regard to *decumana*, *Shaddock* is sweeter and *Matheepala* is sourer, but both of them are characterised by bitterness. All the fruits examined are good sources of vitamin C, the sweeter varieties being better than the sourer type.

Other chemical characteristics which are capable of distinguishing between the species were looked for in the peels and rags of the fruits. The following table gives particulars about the chemical composition of the peels expressed as percentage.

TABLE II

	Batavias	*Kamalas*	*Dabba*	*Shaddock*	*Matheepala*
Acids as citric acid ..	0·88	0·72	4·23	1·67	3·84
Crude fat	0·26	0·23	0·27	0·27	0·29
Sugar (as invert sugar) ..	4·22	4·53	0·84	4·54	2·05
Starch (as invert sugar) ..	6·21	6·42	4·83	6·55	5·22
Proteins	2·48	2·23	2·21	1·51	1·82
Crude fibre	2·34	2·48	3·23	3·86	3·42
Total solids	21·24	22·34	23·21	24·12	24·93
Mineral matter	1·94	2·08	1·84	2·08	1·79
Potassium as K_2O ..	0·39	0·42	0·32	0·43	0·28
Phosphorus as P_2O_5 ..	0·22	0·25	0·10	0·20	0·12

It may be noted that even in the peels, the sweeter varieties contain more sugar and less acid as compared with the sourer fruits. Further the former have more potash and phosphoric acid.

In the course of this work special attention was paid to the existence of crystalline compounds in the peels and rags. The fresh rags were directly extracted with alcohol whereas the peels were dried and subjected to a preliminary extraction with petroleum ether or ether before treatment with alcohol. From these alcoholic extracts hesperidin was found to be present in the two varieties of *aurantium* and of *medica*, wheras *naringin* was present in the *decumana* varieties. Thus the bitter taste of the *decumana* species is associated with naringin, and though hesperidin is chemically closely related, its taste is not so markedly bitter. In this connection it may be mentioned that there has been difference of opinion regarding the species to which *Matheepala* belongs. According to Gamble it belongs to *C. decumana*, though some others would place it under *C. medica*. The classification of Gamble is supported by the isolation of naringin from the peels and rags of this fruit, since this bitter principle is characteristic of the *decumana* species. In regard to the petroleum and ether extractable matter it was found to consist usually of essential oils, resins and carotenoids. But from the *Kamalas* a pale yellow crystalline compound has been obtained in a very small yield. When crystallised from aqueous methyl alcohol it sinters at 83° and melts at 125–26° and has the formula $C_{21}H_{22}O_8, H_2O$. It has six methoxyl groups and is a completely methylated compound. On demethylation with hydriodic acid it forms a crystalline substance decomposing above 320°. The corresponding acetate melts at 238–40°. The behaviour of the hydroxy compound is that of a hydroxyflavone. It gives a red colour when reduced with magnesium and hydrochloric acid,[1] forms a brown precipitate with neutral lead acetate and is decomposed in an alkaline solution when exposed to air. In these respects it appears to resemble a flavonol.

The original substance thus belongs to the group of completely methylated compounds of the type of tangeretin[2] and nobiletin,[3] isolated from other species of the citrus. Since the new compound possesses properties different from them it is here named ' aurantin ' and the corresponding hydroxy-compound ' nor-aurantin '. When subjected to decomposition with concentrated soda, aurantin yields an acid whose nature is not yet clearly understood.

Experimental

Examination of the rags.—As the rags contained very little of oily matter they were directly extracted with alcohol. They were well crushed in a mortar and boiled with enough methylated spirit for three hours under reflux. The extract was decanted off and the process repeated twice. The combined alcoholic solution was filtered to remove suspended impurities and concentrated under reduced pressure to the consistency of a thin syrup. The residue was filtered with suction while hot and the filtrate was left in the ice-chest for crystallisation. The crystalline solid that separated after a few days was filtered off and washed on the filter with a few drops of dilute alcohol. It was then crystallised from the appropriate solvent—hot absolute alcohol and acetic acid in the case of *Batavia*, *Kamala*, *Naranja* and *Dabba*, and hot water in the case of *Shaddock* and *Matheepala*. The first four yielded hesperidin melting at 251–52° and the last two naringin, the air-dried sample melting at 83°, and when dried at 110° melting at 172°. The identities were confirmed by direct comparison with authentic specimens.

Examination of the peels.—Of the different methods tried, the following gave the best yield of crystalline bitter principles. The dried and powdered peels were extracted with petroleum ether in a Soxhlet until all resinous and oily matter was removed. The residue was dried and extracted twice with boiling methylated spirit, refluxing for two hours each time. The combined extract was filtered and treated with a slight excess of neutral lead acetate in alcohol. After removal of the lead precipitate by filtration, the alcoholic filtrate was heated to boiling and saturated with hydrogen sulphide gas until the excess of the lead salt was precipitated. The lead-free alcoholic solution was then concentrated under reduced pressure until a syrupy residue was obtained. When left in the ice-chest for a few days this residue deposited crystalline material which was subsequently purified by recrystallisations. The same bitter principles were obtained in this experiment as from the rags.

Isolation of aurantin.—The dried and powdered peels of *Kamala* oranges (2·5 kg.) were extracted in lots of half a kilo each with ligroin by heating on

a steam-bath for about 10 hours. The extract which was pale yellow in colour was run off completely and the residue was re-extracted twice with ligroin in the above manner. The combined extract was concentrated by distilling off the solvent from an oil-bath at about 110°. The residue which was highly coloured (yellowish green) due to the presence of carotene and other pigments was boiled with a large excess of methyl alcohol (200 c.c.) and the hot solution filtered. The methyl alcohol insoluble portion was discarded and the alcoholic filtrate concentrated on a water-bath. During this process some resinous matter separated out slowly. The clear alcoholic solution was decanted into another flask and the concentration continued until a volume of about 25 c.c. was obtained, insoluble matter being removed now and then as described above. The residual alcoholic concentrate was diluted with an equal volume of water, heated to boiling, cooled and again filtered from insoluble material. After again concentrating to about 35 c.c. the residue was cooled ; on scratching the sides of the flask with a glass rod an amorphous solid slowly separated. This was filtered off (yield, about 1 g.). It was slightly sticky to the touch and was purified by dissolving in a slight excess of cold methyl alcohol and filtering through a fluted filter to remove colloidal inpurities. After dilution with half its volume of water it was set aside for crystallisation overnight in a loosely covered flask. Fine pale yellow needles separated which appeared quite pure and homogeneous when examined under the microscope. The solid sintered at 83° and melted at 125–26°.

The compound was sparingly soluble in water, moderately soluble in methyl and ethyl alcohol and very easily in acetic acid. It was insoluble in cold dilute alkali and gave no colour with alcoholic ferric chloride. It dissolved readily in cold concentrated sulphuric acid to give a pale yellow solution which did not exhibit any fluorescence. It was only sparingly soluble in concentrated hydrochloric acid in the cold, but dissolved on heating to produce a yellow solution from which a crystalline solid slowly separated out. [Found : C, 59·7 ; H, 6·0 ; MeO, 44·4; $C_{21}H_{22}O_8$, H_2O requires C, 60·0 ; H, 5·7; MeO, 44·3%.]

Nor-aurantin.—Aurantin (250 mg.) was dissolved in phenol (5 g.) and treated with hydriodic acid (d. 1·7, 10 c.c.). The mixture was heated in an oil-bath maintained at 140–50° with a gentle current of carbon dioxide passing through the system. The progress of the demethylation which occupied about half an hour could be easily followed by the marked smell of methyl iodide in the exit tube of the system. After heating for about 2 hours the mixture was allowed to cool. On dilution with water (70 c.c.) a yellow powder was precipitated. The mixture was decolorised by passing

sulphur dioxide through it and subsequently heated to boiling, when the solid dissolved, leaving behind a small amount of a heavy slimy material. The clear solution was carefully filtered in the hot and allowed to cool. The yellow powder that separated was filtered and washed with water to remove traces of phenol. Crystallisation was effected using a mixture of alcohol and acetic acid. A second crystallisation using acetic acid alone gave the nor-aurantin as yellow rectangular rods which when heated turned brown at about 300° and decomposed above 320°. There was no definite melting point or decomposition point; the tube was too dark for any observation above 320°. [Found : C, 56·5 ; H, 3·4 ; $C_{15}H_{10}O_8$ requires C, 56·6 ; H, 3·1%.]

Nor-aurantin was a yellow solid easily soluble in cold dilute alkali, forming a yellow solution and giving with alcoholic ferric chloride a dark olive green colour and with neutral lead acetate a brown precipitate. It was sparingly soluble in alcohol and only moderately in glacial acetic acid. On reduction with magnesium powder and hydrochloric acid in alcoholic solution it gave a red colour. Its solutions in concentrated acids were yellow. An aqueous suspension turned greenish blue on boiling. On adding sodium amalgam to a solution of the substance in absolute alcohol (Bargellini's test) a brown flocculent precipitate was obtained. When treated with 50% aqueous potash and shaken with air it first formed a dark red solution which slowly turned yellowish brown. After 24 hours the original compound was not recovered by acidification. It gave the following colour reactions with buffer solutions:—

p_H 8·0: Dissolves slowly forming a clear yellow solution after shaking for a minute. Turns greenish yellow and becomes deep green in 3 minutes. In 10 minutes pale greenish blue. After 20 minutes slowly changes and becomes pale yellow in 3 hours which is then stable even after 24 hours.

p_H 9·2: Dissolves more rapidly to form a yellow solution. Develops a green tinge in the course of a minute; the colour is stable for 15 minutes and then slowly fades to pale yellow which is stable.

p_H 10·4: Dissolves immediately to golden yellow which persists for an hour. Then it slowly diminishes in intensity (3 hours) and assumes a permanent pale yellow.

p_H 11·6: Immediate yellow solution changing to orange and red within 20 seconds. This colour is fairly stable and in the course of 2 hours changes to a deeper yellow which persists after 24 hours.

p_H 12·8: The red colour is deeper and is formed more quickly. It also changes more rapidly to yellow.

The hexa-acetate of nor-aurantin was prepared by boiling with sodium acetate and acetic anhydride for 4 hours. The solid that separated on pouring the mixture into excess of cold water and leaving overnight was filtered, washed with water and crystallised from alcohol-acetic acid mixture. A second crystallisation from acetic acid gave the acetate as fine needles melting at 238–40° with slight sintering at 231°. [Found : C, 57·0 ; H, 4·0 ; $C_{27}H_{22}O_{14}$ requires C, 56·8; H, 3·9%.]

Summary

The important citrus fruits (oranges) of the Northern Circars belong to three species: (1) *C. aurantium*, (2) *C. medica*, (3) *C. decumana*. Their chemical compositions support their classification as the sweet, the sour and the bitter types. In the peels and rags of the first two types hesperidin is present whereas naringin occurs as the characteristic crystalline bitter principle of the varieties of the *decumana*. From the peels of *Kamala* (*C. aurantium*) a new substance has been obtained by extraction with ligroin and named aurantin. It is a completely methylated compound of the type of tangeretin and nobiletin. Its properties and reactions along with those of nor-aurantin are described.

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STUDIES ON SOILS—PART II: A MICROSCOPIC STUDY OF THE BEHAVIOUR OF THE BLACK COTTON SOIL IN SALT SOLUTIONS*

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1. Introduction

In Part I of this series the ascent of water and solutions of some salts of lithium, sodium and potassium through columns of black cotton soil was discussed. It was found that of the salts experimented with, the carbonates of lithium and sodium caused a conspicuous decrease in the rate ascent of water. This led us to examine under the microscope the behaviour of the particles of the black cotton soil when placed in drops of various solutions.

It may be mentioned that the black or "regur" soils of India cover most of the cotton-growing tracts of the country. They are rich in clay (up to 70% consists of clay and fine silt) and in calcium (up to 4%).† During the wet season or after irrigation the field assumes an uneven appearance due to swelling of the soil. The water-holding capacity is very high. After the clear season sets in the soil crust becomes dry rapidly. Shrinkage during this process brings about the characteristic large cracks or the soil "ploughs itself" as the farmer would say. Though sticky and difficult to work when wet, on drying the soil becomes quite friable, unlike other clayey soils which become hard like brick. When dry, the soil absorbs moisture from the atmosphere so that the water lost by evaporation by day during the clear season is regained at night by absorption.

Before proceeding to discuss our results, reference may be made to the investigations of Annett[1] and Harrison and Ramaswamy Sivan[2] on the black cotton soil and to some recent work of Puri.[3, 4] Annett concluded from his examination of a number of black cotton soils that their colour is mainly due to the presence of titaniferous magnetite and small quantities of soluble humus. Harrison and Sivan, on the other hand, after a more extensive investigation of the subject, found that not all black cotton soils contain

* Read before the Annual Meeting of the Indian Academy of Sciences held at Nagpur on the 25th December 1941.

† "Soils of the Bombay Presidency," by Rao Bahadur D. L. Sahasrabuddhe, *Bulletin No.* 160 *of* 1929, *Department of Agriculture, Bombay.*

titaniferous magnetite and that the black colour and peculiar physical properties of these soils are associated with (*a*) compound particles of low specific gravity in which the binding material is probably a colloidal hydrated double iron and aluminium silicate and (*b*) an organic compound of iron and aluminium. Harrison and Sivan also found that on ignition the black colour turns to a bright reddish brown colour and the soil loses weight due to the destruction of the contained organic matter (humus) and the loss of combined water. These observations are of great interest from the point of view of the present paper.

It may also be mentioned that the effect of sodium carbonate in making the soil water-logged and difficult to work is well known. Puri[4] has shown that a lining of sodium carbonate along beds of canals prevents the seepage of water. In another interesting paper[3] Puri has discussed the use of lithium and sodium ions for "auto-disintegrating" the colloidal fraction of a number of soils.

2. *The Microscopic Examination of the Behaviour of Particles of Black Cotton Soil in Solutions*

Soil particles passed through a piece of muslin were used in these experiments. A small quantity of the soil was placed on the microscope slide. To avoid crowding of the particles they were suitably scattered on the slide. Light from a small point source was focussed from above by a suitable condenser on the spot to be examined. The beam of light was incident at an angle of 85°, so that the illuminated particles could be seen against a dark background. A few drops of water or the solutions were introduced at the illuminated spot and the microscopic objective swung into position for examining the effect of the liquid medium on the appearance of the particles. A magnification of about 70 was used for taking the micro-photographs with the help of a photographic attachment. The latter was provided with a reflex arrangement and an eye-piece at the side so that even while photographing the slide could be under observation.

Effect of Lithium Carbonate.—When placed in a drop of distilled water and examined under the microscope the particles of soil are seen to consist of fragments of various minerals with sharp boundaries; most of these are covered with a gum-like layer of varying thickness, while a few are particles of quartz or other transparent minerals. Some of the transparent particles appear to have only a thin coating of the colloidal material. After the lapse of several minutes some of the particles show *very slight* swelling but no other change. Fig. (*a*) in Plate I shows the appearance of soil particles in water. When a drop of lithium carbonate solution is added, a *very rapid*

and conspicuous swelling of the particles immediately sets in. The maximum swelling is attained in a drop saturated or nearly saturated with lithium carbonate. Fig. (*b*) in Plate I shows the appearance of the swollen particles in a drop of lithium carbonate solution. The ratio of the size *after* swelling to that *before* swelling is seen to depend upon the thickness of the colloidal coating around the particle. If the swelled material is agitated with a pin or otherwise mechanically, it gets detached in pieces from the particle and gets scattered, leaving the particle with an appearance similar to that before the addition of lithium carbonate. It thus appears that it is only the colloidal coating which undergoes swelling. When the colloidal cover is thick the swelling is indeed several times the original size of the particle. This will be clear from Figs. *e, f* and *g* of Plate I, where the swelling of a single particle is shown. The mean radius of the particle has roughly doubled itself in the course of four minutes.

It is well known that when a mass of the soil is kneaded with water up to the sticky point, a plug of the kneaded soil when inserted in a glass tube can support a column of water without much drainage occurring. Fig. *c*, Plate I, shows the appearance under the microscope of a smudge of kneaded soil. It is seen that the interspace between the bigger particles is filled with broken down debris of smaller particles, thus rendering the soil less permeable to water. That the kneaded soil can be rendered still less permeable under the influence of lithium carbonate is seen clearly from Fig. *d*, Plate I, where the additional effect of swelling is visible.

We may now consider the effect of lithium carbonate on Poona soil which has turned red after being subjected to prolonged heating. It is found that even a saturated solution of lithium carbonate has no *swelling* action on the soil particles. On ignition the air-dry soil lost 14% of its weight. Of this, 10% represents loss of organic matter and combined water and 4% represents the hygroscopic moisture. The absence of swelling in lithium carbonate must therefore be due to the destruction of the organic colloidal coating during heating.

After making the above observations an experiment was made on the ascent of a 0·5% solution of lithium carbonate through unheated and heated samples of black cotton soil packed in glass tubes according to the standard method described in Part I. Four replications were used as usual. Table I gives the result of this experiment.

There is hardly any ascent in the unheated soil; negative values are due to the upper edge of the wet column being below the level of the solution outside the tube. The actual rise above this level is only 0·1 cm. even

TABLE I

Ascent of Lithium Carbonate Solution (0·5%) in Poona Soil (a) before heating and (b) after heating

Time after commencement of experiment	Before heating		After heating	
	Mean height of wetted column in cm.	C.V.	Mean height of wetted column in cm.	C.V.
10 mts.	−1·0	0	5·5	15
20 „	−0·9	15	6·0	13
30 „	−0·8	36	6·4	12
40 „	−0·7	40	6·6	12
1 hour	−0·5	36	6·9	11
2 hours	−0·4	35	7·4	11
3 „	−0·2	100	7·7	11
4 „	0·1	0	8·1	11
6 „	0·1	0	8·5	10
8 „	0·1	0	8·7	10
14 „	0·1	0	9·3	9

after 14 hours. On the other hand, in the heated soil there is a rapid rise of the solution and the height of the wet soil is 9·3 cm. in 14 hours. The effect of heating in destroying to a large extent the colloidal coating of the soil particles and the consequent increase in the permeability of the soil even to lithium carbonate are thus brought out strikingly by the results quoted in Table I. It may be remarked that in another experiment with unheated and heated soils, water also was found to move upwards more rapidly in the heated soil than in the unheated soil. In this connection reference may be made to a recent note entitled " Fired soil as fertilizer ".* The decrease in the colloidal content of the soil on heating was also tested by another method. Earlier work at Poona referred to at the beginning of Part I showed that when a soil containing only hygroscopic moisture is exposed fully to the atmosphere on a clear day it loses moisture by evaporation during day up to about 2 P.M. and later in the evening and night reabsorbs from the atmosphere practically all this moisture. Thus air-dry soil will attain its maximum weight early in the morning and its minimum weight in the afternoon. The difference between these weights shows the diurnal exchange of moisture between the soil and the atmosphere. Soils containing a large amount of colloidal matter exchange more water vapour with the atmosphere than those with a smaller amount. This experiment was made with the unheated and heated soils during the period 17th to 23rd

* *Indian Farming*, October 1941, 2, No. 10.

November 1941. The mean values of the maximum weight in the morning and the minimum weight in the afternoon of the unheated and heated soils are given in Table II.

TABLE II

	Maximum weight of the soil at the minimum temperature epoch	Minimum weight of the soil at the maximum temperature epoch	Difference indicating diurnal exchange with atmosphere
	gr.	gr.	gr.
Unheated ..	21·71	20·97	0·74
Heated ..	18·31	17·93	0·38

The amount of moisture exchanged is found to decrease to 50% after the heat treatment.

3. A Comparison of the Effect of Lithium, Sodium, Potassium, Cæsium and Ammonium Carbonates

An examination of particles of black cotton soil in solutions of lithium, sodium, potassium, cæsium† and ammonium carbonates respectively is very instructive. As the weight of the metallic radical increases the swelling effect is seen to decrease very rapidly. Thus the effect is very pronounced in lithium carbonate, less so in sodium carbonate, perhaps a trace in potassium carbonate and practically absent in cæsium carbonate. Figs. *a*, *b* and *c* of Plate II show the behaviour in lithium, sodium and potassium carbonates. Fig. *d* shows the effect in ammonium carbonate solution. There is a trace of swelling and this is accompanied by the evolution of the bubbles of ammonia gas which are visible in the micro-photograph.

4. Effect in Oxalic Acid and Various Oxalates

In the case of the carbonates it is not possible to compare their swelling effects with that in carbonic acid which is not stable in water. Even in water under compressed carbon dioxide the amount of the CO_3 ion is very small when compared to that in solutions of the carbonates.

In the case of oxalic acid and the oxaltates such a comparison is, however, possible. The micro-photographs of soil particles under water, oxalic acid, sodium oxalate and potassium oxalate are shown in Figs. *e*, *f*,

† Later, rubidium carbonate was also tried; it comes between potassium and cæsium as regards its swelling effect.

g and *h* respectively of Plate II. It is remarkable that of all these substances the solution of *oxalic acid shows the maximum swelling*. The effect of sodium oxalate solution is similar to that of sodium carbonate, but much less than that of oxalic acid solution. Going further in the series one finds that particles in potassium oxalate solution show little swelling and that particles in ammonium oxlate are very similar to those in water. Thus the H-ion in oxalic acid is much more efficient in causing the swelling of the colloidal cover of the soil particles than the $Na^{\cdot}$ or $K^{\cdot}$ ions. This result is indeed very interesting.

We have similarly examined the effects of tartaric acid and sodium and potassium tartarates, formic acid and sodium formate and citric acid and sodium citrate. In these cases also the acid is a more efficient swelling agent than the salt. The study of the phenomenon in the case of other related series of compounds is in progress.

5. Swelling in Solutions of a Number of Organic Acids

It was possible to secure pure samples of tartaric, oxalic, citric, lactic, malic and oleic acids. Figs. *a* to *f* of Plate III show the extent of swelling in saturated solutions of the first five acids and in oleic acid in the order in which they are mentioned above. It is obvious that tartaric, oxalic, citric and lactic acids are quite efficient as swelling agents. The effect in malic and oleic acids is not very noticeable.

6. Summary and Conclusions

In this paper the swelling of the colloidal material in black cotton soils in solutions of a number of substances has been described. Lithium carbonate is found to be the most efficient swelling agent amongst the substances tried so far. In any group of related compounds like acid and its alkali salts it is found that the acid causes much more swelling than the salts. Amongst the salts the swelling decreases rapidly in the order Li, $Na^{\cdot}$, $K^{\cdot}$, Rb, Cs.

The effect of prolonged heating is to destroy the organic colloids covering the particles. This leads to the absence of swelling even in lithium carbonate solution and a marked increase of permeability.

The paper summarises the result of a preliminary survey of these related phenomena in the case of the black cotton soil. A more detailed and systematic investigation in the case of a number of typical Indian soils, particularly from the point of view of applications to agricultural practice, is in progress.

The physical and chemical aspects of swelling will be discussed in the next part, in the light of the detailed experiments on the effect of concentration of the salt on the movement of the solution through the soil.

Our best thanks are due to the Director-General of Observatories for providing the necessary facilities for this investigation.

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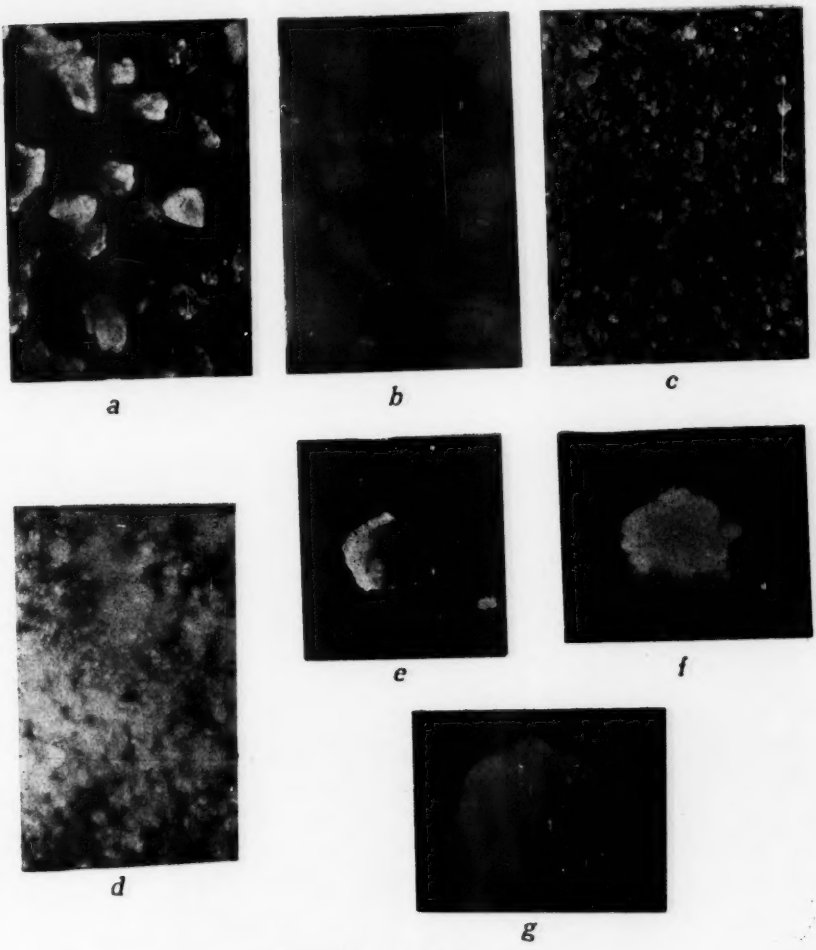
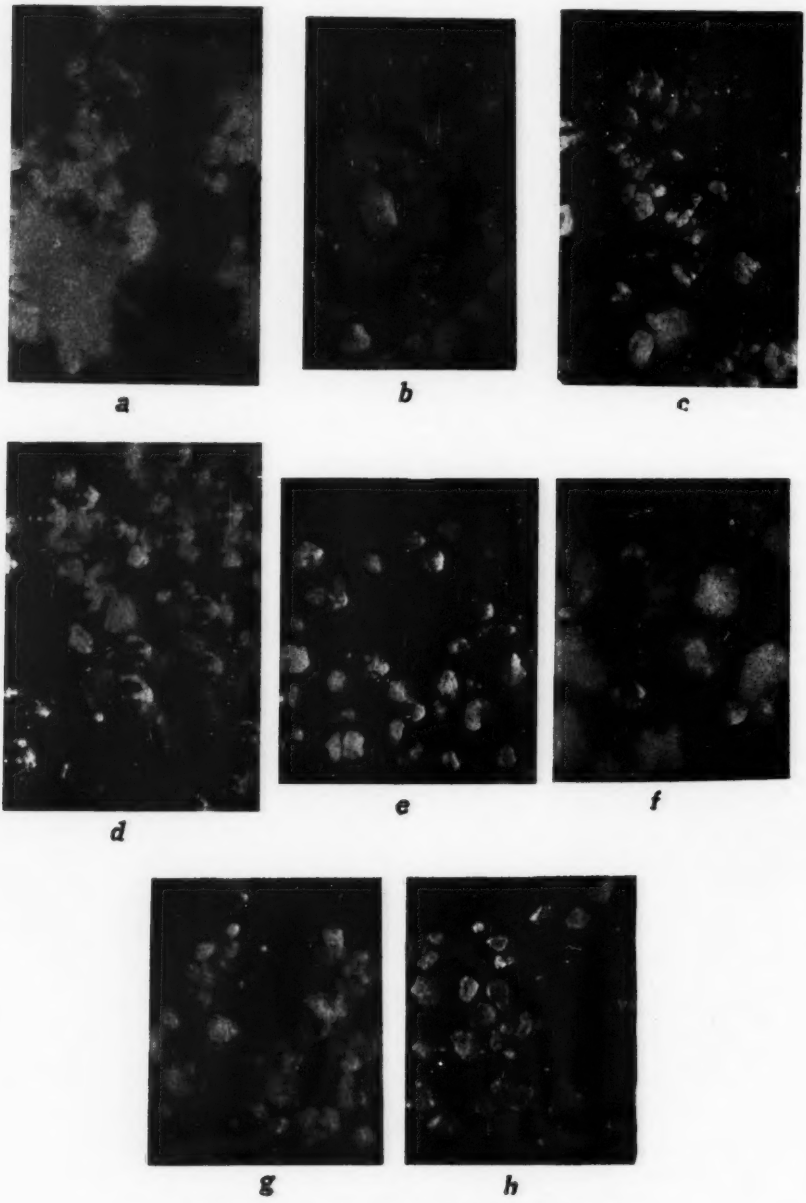


Particles of Poona soil

(*a*) in water
(*b*) in lithium carbonate solution
(*c*) in water after kneading, and
(*d*) in lithium carbonate solution after kneading

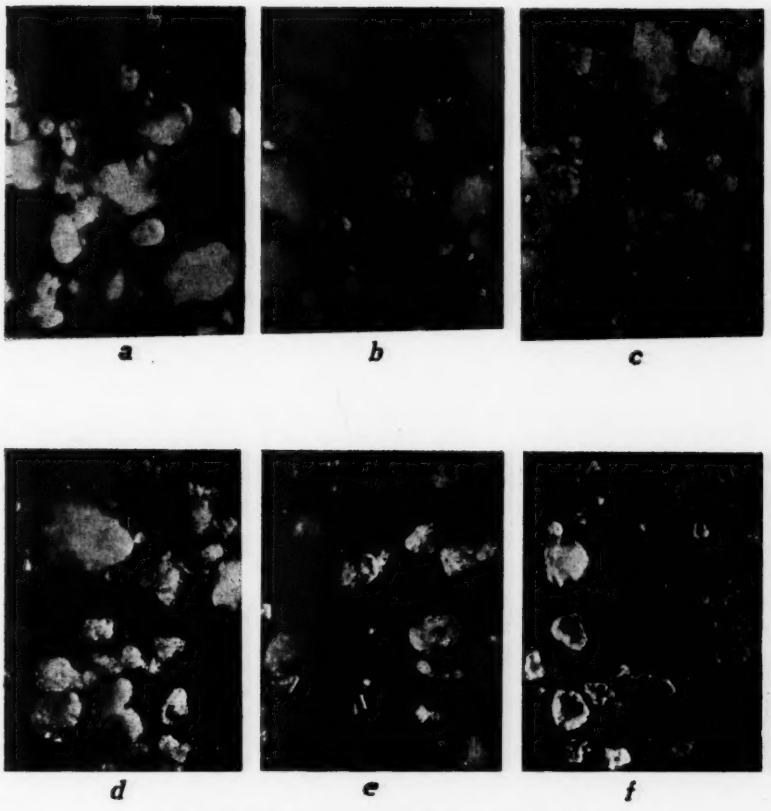
A single particle of Poona soil

(*e*) in water
(*f*) 1 minute after adding a drop of saturated lithium carbonate solution, and
(*g*) 4 minutes after adding a drop of saturated lithium carbonate solution



Particles of Poona soil in a drop of

(*a*) lithium carbonate solution
(*b*) sodium carbonate solution
(*c*) potassium carbonate solution
(*d*) ammonium carbonate solution
(*e*) water
(*f*) oxalic acid solution
(*g*) sodium oxalate solution, and
(*h*) potassium oxalate solution



Particles of Poona soil in a drop of

(*a*) tartaric acid solution
(*b*) oxalic acid solution
(*c*) citric acid solution
(*d*) lactic acid solution
(*e*) malic acid solution, and
(*f*) oleic acid

CHEMICAL EXAMINATION OF INDIAN LICHENS

Part VI. Constitution of Erythrin

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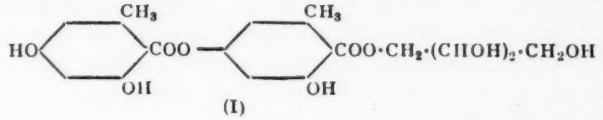
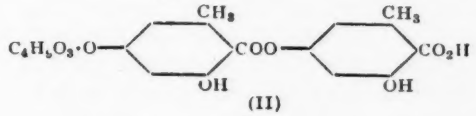
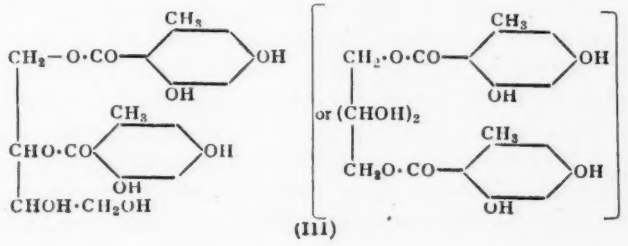
In previous communications relating to Indian lichens the occurrence of erythrin in *Roccella montagnei* along with roccellic acid, lecanoric acid, montagnetol, orcinol and erythritol was recorded.[1] This compound has also been known to be the chromogen of many lichens belonging to the *Roccella* genus (*e.g.*, *Roccella tinctoria*) and also in certain others like *Lecanora tartarea*, *Dendographa leucophæa*, *Aspicilia calcarea*, *Parmelia olivetorum* and *Evernia furfuracea*.[2] Its constitution has remained so far unsettled, though its molecular formula is definitely known to be $C_{20}H_{22}O_{10}$, H_2O. From a consideration of its reactions several alternative constitutions were suggested. Hesse[3] was of the opinion that it existed in two easily interconvertible tautomeric forms: (1) the erythrityl ester form (I), (2) the erythric acid form in which the erythrityl group is attached to an ether linkage (II). Zerner[4] criticised this idea of tautomerism as untenable and the formulæ as unsatisfactory. After referring to another constitution suggested by Luynes (III) he advocated the adoption of structure (IV) as the most satisfactory. No unequivocal proof has, however, been given so far in support of any of these formulations.



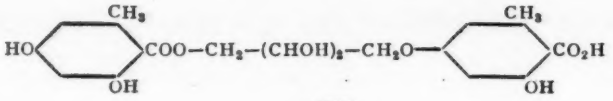
(I)



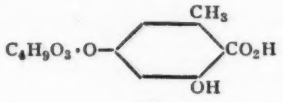
(II)



(III)



(IV)



(V)

The important properties and reactions which these formulæ were intended to satisfy were as follows :

(1) By treatment with baryta, erythrin yielded orcinol, erythritol and carbon dioxide.

(2) By gentler decomposition using boiling water or alcohol picroerythrin was formed along with orsellinic acid when water was employed, and esters of orsellinic acid when alcohols were employed.

(3) Erythrin and picroerythrin were considered to be acidic in nature.

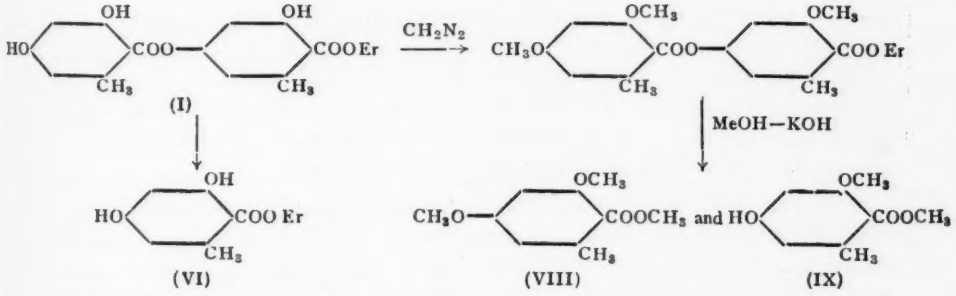
(4) Picroerythrin (also known as erythroorsellinic acid) underwent further decomposition with baryta water into erythritol, orcinol and carbon dioxide and was considered to have formula (V).

Though both formulæ (II) and (IV) explain all these properties and reactions satisfactorily, the occurrence of lecanoric acid along with erythrin was considered in Part I[1] as support for Hesse's formula (II).

A careful examination of a pure sample of erythrin shows that it does not have a free carboxylic group. Although it dissolves fairly readily in lime water and sodium carbonate it is found to be insoluble in sodium bicarbonate. On the other hand, lecanoric acid dissolves readily in aqueous bicarbonate with brisk evolution of carbon dioxide. The feeble acid properties of erythrin are obviously due to the presence of a number of phenolic hydroxylic groups and there is no carboxyl group in the molecule. A sample of picroerythrin obtained by the decomposition of erythrin with water is again found to be non-acidic. It is soluble in water to form a neutral solution and does not give effervescence with sodium bicarbonate. From its melting point and principal reactions it is found to be identical with inactive or racemic montagnetol. By carefully regulating the decomposition of erythrin with water a sample of optically active picroerythrin (*d*-montagnetol) could also be obtained. It is therefore clear that active montagnetol is the first product of decomposition and it subsequently racemises. This close relationship is in accordance with the occurrence of erythrin and montagnetol together in

the lichens. It may be noted here that erythrin exhibits optical activity being dextrorotatory just as montagnetol, and the molecular rotations of the two in acetone solution are very close (montagnetol 3427, erythrin 3376).

The constitution of montagnetol has been recently established as the erythrityl ester of orsellinic acid (VI) from a detailed study of all its properties and reactions[5] and now it is shown that montagnetol and picroerythrin are identical. Hence formula (V) has to be discarded. On account of this and also on account of the fact that erythrin is not a carboxylic acid, the formulæ (II) and (IV) become untenable. The other possibilities, (I) and (III) indicate that erythrin is a neutral compound and contains within the molecule the montagnetol unit. Of these (III) does not contain a lecanoric acid unit and further, on hydrolysis, it may not be expected to yield picroerythrin readily, since both the orsellinic acid units may be expected to be liberated with almost equal facility. On the other hand, formula (I) is free from these objections and explains all the properties of erythrin and its relationship with other compounds satisfactorily. This conclusion has been verified by methylating erythrin with excess of diazomethane and hydrolysing the product. A trimethyl ether of erythrin (VII) is first formed and when it is hydrolysed with alcoholic potash it gives rise to a mixture of esters which has been separated into the methylester of dimethyl orsellinic acid (VIII) and the methyl ester of isoeverninic acid (IX). The esters were also hydrolysed to the corresponding acids. The various stages of the decompositions can be represented as below :



[Er = $C_4H_9O_3$, erythrityl group]

As the result of our detailed study of the components of *Roccella montagnei* and the establishment of the constitutions of montagnetol and erythrin a possible evolution of these substances in the lichen could be suggested. Though orsellinic acid does not occur free in nature, it seems to be obviously the primary product and on account of its instability it does not

survive. A small part of it decomposes to orcinol; but the main bulk seems to be stabilised (1) by conversion into the erythrityl ester, montagnetol, (2) by depside formation as lecanoric acid, and (3) by further esterification of lecanoric acid to produce erythrin. The alternative method for the formation of erythrin by the combination of orsellinic acid and montagnetol is also possible. It could be inferred that under the conditions prevailing in the lichen erythrityl ester formation is largely favoured since lecanoric acid occurs only occasionally and in smaller amounts and the bulk of the components are accounted for by montagnetol and erythrin. It is remarkable however that the aliphatic lichen acid, roccellic acid, is found free and its erythrityl ester has not yet been isolated.

Experimental

Properties of erythrin.—A pure sample of erythrin crystallised from aqueous acetone in the form of bundles of colourless needles melting at 156–57°. It was very sparingly soluble in water and the aqueous solution was neutral to litmus. Though lime water and sodium carbonate dissolved it, it was insoluble in sodium bicarbonate solution. $[\alpha]_D$, + 8·0. It is not markedly bitter in taste.

Preparation of picro-erythrin.—Erythrin (0·2 g.) was boiled under reflux with 20 c.c. of water. Complete solution was effected in about an hour. The heating was, however, continued for one more hour. The solution was then extracted with ether repeatedly in order to remove orsellinic acid and orcinol, and the aqueous solution concentrated on a water-bath. A viscous liquid was first obtained and it underwent change into a crystalline solid on keeping. When recrystallised from a mixture of acetone, ether and benzene, it was obtained in the form of colourless rectangular tablets melting at 156–57°. It gave a purple-violet colouration with ferric chloride and was found to be identical in every respect with racemic montagnetol. The mixed melting point was unchanged.

If the boiling was discontinued as soon as a clear solution was obtained and the solution worked up, *d*-montagnetol, melting at 136°, could be obtained, but it was always accompanied by small amounts of the racemic variety also and purification was very difficult.

Methylation of erythrin—preparation of trimethyl erythrin.—Erythrin (1 g.) was dissolved in anhydrous methyl alcohol (50 c.c.) and treated with excess of ethereal diazomethane in two lots in the course of two days. After the first day as much of the ether as possible was removed by gentle heating and the second lot of ethereal diazomethane added. The solvents were finally distilled off and the semi-solid residue crystallised from methyl

alcohol. It came out in the form of colourless, fibrous needles, which turned to a glassy mass at 110–12° and ran down into a clear liquid at 118–20°. It gave no colour with alcoholic ferric chloride solution and was insoluble in aqueous sodium hydroxide. [Found: CH_3O, 20·8%; required for 3 MeO groups in $C_{23}H_{28}O_{10}$, 20·0%.]

Decomposition of trimethyl erythrin.—Trimethyl erythrin (0·4 g.) was carefully heated with methyl alcoholic potash (4%, 20 c.c.) for two hours on a water-bath, the temperature being kept at about 55°. The solution was diluted with an equal amount of water and repeatedly extracted with ether. When the ether solution was concentrated it yielded a viscous liquid which slowly turned solid on keeping for several hours. It could then be recrystallised from alcohol or benzene, and from the latter it came out as colourless prisms melting at 44–45°. It gave no colour with ferric chloride. [Found: OCH_3, 44·2% ; required for 3-OCH_3-in $C_{11}H_{14}O_4$, 43·3%.] The ether-soluble product was therefore identified as the methyl ester of dimethyl orsellinic acid. A small sample of it was hydrolysed by boiling with 5% aqueous-alcoholic (1 : 1) potassium hydroxide solution for 15 minutes. After leaving the solution overnight it was acidified and repeatedly extracted with ether. The ether extract yielded on evaporation a colourless crystalline solid which crystallised from methyl-alcohol in the form of sheaves of needles and melted at 140–41° with slow decomposition. It gave no colour with alcoholic ferric chloride and was found to be identical with an authentic sample of dimethyl orsellinic acid.

The original aqueous solution obtained from the decomposition of trimethyl erythrin and left after the removal of the ester of dimethyl orsellinic acid by ether extraction, was at this stage acidified and repeatedly extracted with ether. The combined ether extract was shaken with aqueous sodium bicarbonate (solution X) in order to remove any acid that might have been formed. When the ether solution was then evaporated, a semi-solid residue was left. Since the quantity was small, it was directly hydrolysed by heating with 10 c.c. of 5% aqueous potash for 15 minutes on a boiling water-bath and subsequently allowing it to stand at room temperature for 1 hour. It was then acidified and repeatedly extracted with ether. On evaporating the ether solution a crystalline solid was obtained. It was repeatedly washed with benzene. The solid was in the from of colourless rectangular plates and prisms melting with decomposition at 174–75° [Found: -OCH_3, 17·7% ; $C_9H_{10}O_4$ requires for 1-OCH_3, 17·0%.] With alcoholic ferric chloride it gave only a reddish-yellow colour. The substance was therefore identified as isoeverninic acid.

The bicarbonate extract (solution X) was carefully examined as below: It was acidified with hydrochloric acid and repeatedly extracted with ether. From the ether extract a solid was obtained which had an indefinite melting point and which could, however, be separated by treatment with benzene. The benzene-insoluble portion melted at 174–75° and proved to be isoeverninic acid, whereas the benzene-soluble protion melted at 140° with slight decomposition and was found to be dimethyl orsellinic acid.

Summary

The constitution of erythrin has been definitely established. The new important observations now made are as follows: (1) it is not a carboxylic acid ; (2) it is optically active ; (3) picroerythrin is identical with montagnetol ; (4) trimethyl erythrin a compound in which all the phenolic hydroxyl groups are methylated is obtained by the action of diazomethane; (5) on hydrolysis with alcoholic potash the methyl ether yields the ester of dimethyl orsellinic acid and the ester of isoeverninic acid. Consequently, it is concluded that erythrin is the erythrityl ester of lecanoric acid. This is in agreement with the occurrence of lecanoric acid and montagnetol along with erythrin in the lichens.

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REACTIVITY OF THE DOUBLE BOND IN COUMARINS AND RELATED UNSATURATED CARBONYL COMPOUNDS

Part IX. Addition of Cyanoacetamide to Coumarins with Electron-attracting Groups in the 3-Position

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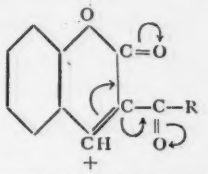
In previous publications on this subject[1] it was shown that amongst compounds having reactive methylene groups only cyano-acetamide adds to the double bond of coumarins, that the addition is considerably accelerated by a nitro-group in the 6th position and that it is retarded by hydroxy and methoxy groups in the 7th position. The reaction is prevented by the presence of alkyl and bromo substituents in the pyrone ring. The results of a few typical experiments on the influence of electron-attracting groups such as the carbonyl, cyano and phenyl, when present in the 3-position, on this addition, are now reported. They could be expected to enhance the reactivity of the coumarin double bond by increasing the cationoid activity of the carbon atom in the 4th position as shown below (I) :



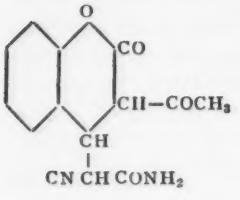
(R=CH_3, C_6H_5, OC_2H_5 or OH)

(I)

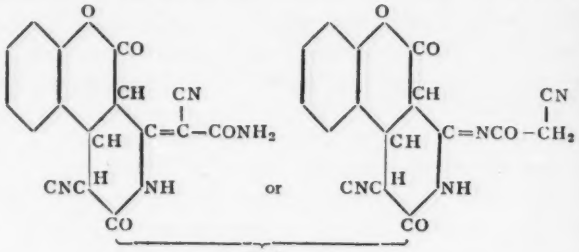
3-Acetyl coumarin reacts fast with cyano-acetamide but the yield of the product (II) is not high owing to the existence of side reactions and the removal of the catalyst (piperidine) involved in partial deacetylation of the acetyl compound. This is supported by the observation that a second addition of piperidine gives increased yields. 3-Benzoyl coumarin is similar though the addition is comparatively much slower. With 3-carbethoxy coumarin the reaction goes further, ring formation taking place and a second molecule of the amide also taking part. From the analytical values formula (III) is suggested for the product and it finds support in the

fact that the compound is devoid of an ethoxyl group. A good portion of piperidine is used up for the formation of the piperidide of coumarin-3-carboxylic acid. Coumarin-3-carboxylic acid behaves like coumarin, forming dihydro-coumarin-cyanoacetamide. This is obviously due to decarboxylation taking place in the course of the reaction. In a similar reaction of this carboxylic acid using cyanoacetic ester no addition takes place, but still de-carboxylation proceeds resulting in coumarin. It is interesting to note that 3-cyanocoumarin reacts much faster and gives much better yields of the addition product than the others. This reaction seems also to be free from complications. 3-Phenylcoumarin does not react to any appreciable extent even when boiled for 60 hours. Though the phenyl group is capable of acting both as an electron donor and as an acceptor, as far as the present reaction is concerned, it resembles alkyl groups and does not seem to be functioning as an electron sink.

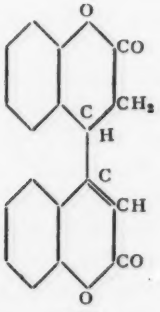
Special mention should be made of the reactions taking place when cyanoacetic ester, malonic ester and acetoacetic ester are employed in the place of cyano-acetamide. 3-Acetyl-coumarin undergoes complex change. No addition product could be obtained, but a sparingly soluble compound is formed which answers to the requirements of dihydro-dicoumarinyl



(II)



(III)



(IV)

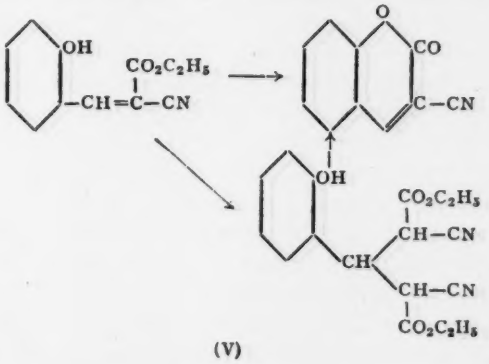
(formula IV). It may arise due to the condensation between themselves of two molecules of the acetyl-coumarin with the subsequent elimination of acetyl groups. This explanation is supported by the observation that the same reaction takes place in the presence of piperidine even when there is no outside additive agent. Such a reaction has not been noticed in the case of other coumarins. 3-Cyanocoumarin, being the most reactive, forms an addition product with cyano-actic ester and not with others. The rest of the coumarins studied do not form addition products with these esters.

Experimental

Preparation of the required coumarins

3-Acetyl-coumarin,[2] 3-benzoyl-coumarin,[3] and 3-carbethoxy-coumarin,[4] were easily prepared by Knoevenagel's method using salicylaldehyde and the appropriate ketonic ester. Coumarin-3-carboxylic acid[4] was obtained by hydrolysing the ester with aqueous alkali. For the preparation of small quantities of the acid this method seems to be the most convenient.

3-Cyanocoumarin was first prepared by adopting the indirect method of Bechert[5] in which salicylidine-bis-cyanoacetic ester is treated in warm alcoholic solution with hot alcoholic potash and the resulting potassium salt is decomposed with dilute sulphuric acid. Knoevenagel and Arnot[3] reported the formation of salicylidine-bis-cyanoacetic ester melting at 139°-40° by the combination of salicylaldehyde and cyanoacetic ester in equimolecular proportions in the presence of piperidine as catalyst, the condensation taking place at room temperature. On repeating this reaction at the laboratory temperature of Waltair (about 28°), as given below, a 25–30% yield of cyanocoumarin could be obtained. When the reaction was carried out at 10—15° which may approximate to Knoevenagel's conditions



(V)

the bis-cyanoacetic ester was formed as the main product. The course of the reaction may be represented as below (V) :

To a mixture of salicylaldehyde (2 c.c.) and cyanoacetic ester (2 c.c.) were added 5 drops of piperidine. The resulting mixture became quite warm and red in colour. After cooling under the tap the reaction was allowed to proceed at the room temperature for four to five hours by which time the mixture set to a solid mass. It was then treated with a small volume of alcohol and thoroughly stirred. The resulting solid was filtered and washed successively with a small volume of alcohol, a small quantity of water and finally with alcohol. It then melted at 182–84°. After recrystallisation from alcohol it appeared as rectangular prisms and prismatic needles and the melting point rose to 185–86°. The yield was 30% of the theoretical. [Found : C, 70·7; H, 3·2; $C_{10}H_5O_2N$ requires C, 70·2; H, 2·9%.]

When, however, two molecular proportions of cyanoacetic ester were employed for one of the aldehyde and the reaction carried out at the laboratory temperature the product was entirely the *bis*-compound which when recrystallised from alcohol melted at 140–41° (yield 60%).

3-Phenyl-coumarin[6,7] was made using salicylaldehyde, sodium phenyl-acetate and acetic anhydride (Perkin's reaction), or the ethyl ester of phenyl-acetic acid and piperidine (Knoevenagel's method). For the preparation of small quantities, the second method is quite satisfactory though the yield is poor.

Addition of Cyanoacetamide

3-*Acetyl-dihydro-coumarin*-4-*cyanoacetamide* (II).—As a typical example of the general addition reaction the one involving acetyl-coumarin and cyano-acetamide is given below in detail.

3-Acetyl-coumarin (4 g.) and cyano-acetamide (2 g.) were dissolved in alcohol (50 c.c.) and a few drops of piperidine were added and the solution kept just boiling. A bulky yellow crystalline precipitate was formed; the reaction seemed almost complete in ½ hour. The precipitate was filtered off and washed thoroughly with water and hot alcohol (yield 1·2 g.). On further boiling of the mother-liquor for 4 hours a small additional quantity of a deeper coloured product was obtained. If, however, a few drops of piperidine were added before the second boiling, the yield of the product was practically doubled. The substance was sparingly soluble in most organic solvents and moderately soluble in pyridine from which it crystallised out as colourless elongated rectangular plates. It began to turn dark pink at about 240° and shrink at 290° and it finally decomposed at 295°.

A sample which was crystallised from pyridine and washed well with water and hot alcohol and dried *in vacuo* at 120° gave the following analytical figures : C, 61·3; H, 4·4; N, 10·8; $C_{14}H_{12}O_4N_2$ requires C, 61·8; H, 4·4; N, 10·3%.

3-Benzoyl-dihydro-coumarin-4-cyanoacetamide

3-Benzoyl-coumarin yielded an yellow coloured product in about the same yield as above after boiling for 6 hours. There was no rapid precipitation as in the case of acetyl-coumarin. Only after leaving overnight a collection of hard yellow crystals was obtained and they were sparingly soluble in alcohol, ether, benzene and acetone. From boiling pyridine the substance crystallised as light yellow rhombic prisms. It sintered at 308° and finally melted with decomposition at 315° [Found: C, 68·8; H, 4·3; N, 8·8 ; $C_{19}H_{14}O_4N_2$ requires C, 68·3; H, 4·2; N, 8·4%.]

Compound (III) from 3-carbethoxycoumarin

The product from 3-carbethoxy-coumarin was obtained in the form of rhombic plates and needles on crystallising from pyridine and it did not melt below 360°. Regarding its solubility in organic solvents it resembled the other compounds described above. Yield, about 15%. [Found : C, 59·1 ; H, 2·8 ; N, 17·0 ; $C_{16}H_{10}O_4N_4$ requires C, 59·6 ; H, 3·1 ; N, 17·4%.]

When tested for the presence of (OC_2H_5) group by the micro-Zeisel method, the compound did not respond.

In the case of this ester the poorness of the yield may partly be accounted for, by the formation of the piperidide, thereby the catalyst being removed. When an alcoholic solution of the ester is treated with a few drops of piperidine only and boiled, no dihydrodicoumarinyl is produced; but a small amount of the piperidide could be isolated. This piperidide which is useful as a drug can be readily made in good yield by the following procedure, though previous workers employed the less easily available acid chloride for the purpose. The compound is irritant and bitter but not pungent to the taste (compare piperidide of cinnamic acid).

Equimolecular quantities of coumarin-3-carboxylic ester (2 g.) and dry piperidine (1 c.c.) were dissolved in 30 c.c. of toluene and the resulting solution refluxed for 3 hours. On cooling the piperidide crystallised out. M. P. 179°; yield, 1 gm. (*cf.* Merck's *Janrberichte*, 1936, p. 98).

3-Cyano-dihydro-coumarin-4-cyano-acetamide

3-Cyano-coumarin added on cyano-acetamide producing an almost quantitative yield. The product crystallised out as colourless flat needles

from pyridine, being sparingly soluble in other organic solvents. It did not melt below 360°. [Found : C, 60·7 ; H, 3·5 ; N, 17·0 ; $C_{13}H_9O_3N_3$ requires C, 61·2 ; H,3·5 ; N, 16·5%.]

Other reactions

Formation of Dihydro-dicoumarinyl (IV).—3-Acetyl-coumarin (1 g.) was dissolved in alcohol and piperidine (3 drops) added. When the resulting solution was refluxed for 3 hours, a pale yellow product separated out which was filtered, washed with a little water and finally with alcohol and recrystallised from pyridine. The substance crystallised as colourless narrow rectangular plates melting at 293° (decomp.). Yield 0·5 g. It is not soluble in ether and alcohol and is moderately soluble in hot pyridine, nitrobenzene and glacial acetic acid. It does not contain nitrogen and does not give a phenylhydrazone. It is insoluble in cold aqueous potash but dissolves on boiling. From this solution it could be recovered by acidification. [Found : C, 74·0 ; 74·3 ; H, 4·0 ; 3·9 ; $C_{18}H_{12}O_4$ requires C, 74·0 ; H, 4·1%.]

When pyridine was used instead of piperidine in the above reaction, there was no condensation. Also when malonic, acetoacetic and cyanoacetic esters were used in conjunction with piperidine the same-dihydrodicoumarinyl was obtained.

3-*Cyano-dihydro-coumarin*-4-*cyano-acetic ester*

3-Cyano-coumarin (0·6 g.) was dissolved in alcohol, cyanoacetic ester (0·3 c. c.) added along with three drops of piperidine and the whole refluxed for 4 to 5 hours when an yellowish crystalline precipitate was obtained. It was filtered off ; a further quantity of the same substance could be obtained when the mother-liquor was left overnight (yield 0·6 g.). The crude product which was washed well with water and a small quantity of alcohol, was crystallised from alcohol in which it was moderately soluble. It came out as colourless needles melting at 247-48°. [Found: C, 63·1; H, 3·9; N, 10·4 ; $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2; N, 9·9%.]

The same compound was obtained when a solution of salicylidene-*bis*-cyanoacetic ester in alcohol was treated with three drops of piperidine and refluxed on the water-bath for 5 to 6 hours.

Summary

Addition of cyanoacetamide to coumarins having substituents in the 3-position, such as the carbonyl, cyano and phenyl which are electron-attracting, has been studied. Unlike alkyl groups and bromine atoms they do not in general inhibit addition. The following coumarins have been

employed : (1) 3-acetyl-coumarin, (2) 3-benzoyl-coumarin, (3) 3-carbethoxy-coumarin, (4) coumarin-3-carboxylic acid, (5) 3-cyano-coumarin, and (6) 3-phenyl-coumarin. The speed of the reaction and the yield of the product depend upon (*a*) the activating capacity of the substituent group and (*b*) the readiness with which it can be eliminated under the experimental conditions. Compounds (1) and (2) give poor yields of the products; (3) combines with 2 molecules of cyano-acetamide ; (4) resembles coumarin due to ready decarboxylation; (5) reacts without complications ; (6) does not react. Among other additive compounds tested cyanoacetic ester reacts satisfactorily with 3-cyano-coumarin. 3-Acetyl-coumarin seems to undergo polymerisation and deacetylation to form dihydro-dicoumarinyl in the presence of piperdine.

Convenient methods for the preparation of 3-cyanocoumarin, coumarin-3-carboxylic acid and its piperidide have been investigated.

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RAMAN SPECTRA OF CRYSTALS EXCITED BY THE MERCURY RESONANCE RADIATIONS

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1. Introduction

Most of the investigations so far published on the Raman spectra of crystals have been made with 4047 and 4358 radiations of the mercury arc. As early as 1931, however, Rasetti developed a technique which enabled the 2537 radiations in the ultra-violet to be used with signal success in this field of research. A quartz arc of the Heraus type, 25 cm. long and 2·5 cm. in diameter, was employed and the electrodes were cooled by immersion in running water. The discharge was deflected towards the walls of the tube nearest the crystal by the field of an electromagnet. These arrangements prevented the 2537 radiations which were strongly emitted by the luminous mercury atoms being re-absorbed by the cooler mercury vapour near the walls. The light scattered in the crystal was filtered by a column of mercury vapour at room temperature placed within the spectrograph. This practically cut off the intense 2537 radiations from the scattered light, thereby avoiding the fogging of the photographic plate and consequent obscuration of the Raman lines. Rasetti worked with several crystals, *viz.*, quartz, ice, gypsum, anhydrite, barite, fluorite and rocksalt. He used a Hilger E. 315 Quartz spectrograph giving a dispersion of 130 wave numbers per mm. The exposures necessary ranged from 10 minutes in the case of calcite to 5 hours for rocksalt.

Rasetti's technique is, of course, applicable only with crystals which are transparent to the 2537 radiations. But for such crystals it is convenient and extremely efficient. The intensity of the 2537 radiations is so great compared with that of the adjoining 2535 and other radiations of the mercury arc that these may be completely ignored as possible exciters of the Raman effect. The high intensity and large scattering power of the 2537 radiations coupled with their elimination from the scattered light enable even small crystals to be successfully employed. The technique is particularly useful in recording Raman lines with small frequency shifts, as these

are liable to be completely obscured in the spectra unless the exciting radiations are suppressed. It is a useful circumstance that the region between 2535 A.U. and 2483 A.U. in the spectrum of the water-cooled arc is completely free from lines and affords a clear region for observing the anti-Stokes excitations over a great range of frequencies. The field of wavelengths greater than 2537 A.U. in the spectrum is less satisfactory as there are fairly strong mercury radiations at 2564, 2576 and 2603 A.U., besides several weaker intermediate lines. These are liable to be recorded on strongly exposed plates if parasitic illumination be present, and the possibility of their being mistaken for Raman lines or of masking such lines when actually present is a potential source of error which should be borne in mind. The observation of the anti-Stokes exitations which are recorded in a clear field is a useful check against errors arising in this way.

The present investigation was undertaken with the intention of using the Rasetti technique for systematic studies and especially for observations with single crystals variously orientated with reference to the directions of incidence and scattering. The utility of the method in working with small crystals, its ability to record very faint Raman lines, and its capacity to exhibit variations in the spectra with crystal orientation have been fully established by the research. In view of the author's work having had to be temporarily suspended, it has been thought desirable to record the results so far obtained.

2. *Experimental*

A small Heraus quartz mercury arc 5 cm. long and 1·5 cm. in diameter which was available was employed in the present investigation. The arc was placed upon a stand and dipped in a trough of water to such a depth that the electrodes were under water. The water in the trough was allowed to overflow continuously and the electrodes were thus kept cool. The discharge was deflected to the upper wall of the arc by a small electromagnet. As no quartz condenser was available, the crystal was placed just above the arc to illuminate it as intensely as possible. The distance from the arc to the crystal was so adjusted as to prevent any appreciable rise in the temperature of the crystal. A screen of mercury vapour was placed in the path of the scattered light so as to absorb the 2537 radiations before they reached the photographic plate. The spectrograms were recorded by a Hilger Intermediate quartz spectrograph $f_d = 38$ cm. with a slit 20 μ wide, the dispersion being 222 wave numbers per millimetre in the region of 2537. Though the instrument is a comparatively small one it gives excellent results. The Ilford special rapid plates employed were sensitized for the ultra-violet by a 1% solution of citric acid in alcohol. The

exposures lasted from 15 to 40 hours depending on the size and nature of the crystals used and the size of the faces available. The plates were measured under a Hilger cross-slide micrometer.

3. Results

Quartz (SiO_2). See Table I.

The Raman spectrum of quartz has been studied by numerous investigators. A detailed discussion of the literature will be found in a recent paper by Saxena. A clear crystal of quartz having well-developed side faces about 8″ long and 2″ thick was selected for the present investigation. A well-exposed spectrum could be recorded in about 6 hours, but a longer exposure of 40 hours was given to get out the weakest lines. The spectrogram reproduced in the plate shows that all the Raman lines have been recorded, while the weaker mercury lines do not appear on the plate. The frequency shifts recorded by Saxena and Nedungadi have all been confirmed in the present investigation. The smaller dispersion available has however prevented the close doublets being resolved. The weak line with a frequency shift of 140 wave numbers which was recorded in the spectrum plates obtained by Saxena and Nedungadi at this Institute by the 4358 excitation but which was not reported by them is also confirmed by the present work. A new group of weak lines having wave number shifts 886, 901, 931 and 940 has also been detected. These are probably to be explained as octaves and combinations of the fundamental Raman frequencies.

Alumina (Al_2O_3)

The Raman effect in alumina is of considerable interest in view of its relation to the fluorescence spectrum of ruby. It has been studied by Hibben (1932), Deutschbein (1932) and recently also by (Miss) Anna M. Mani (1942) in this laboratory who found that the lines appear only weakly in the spectra obtained with the 4358 radiations of the mercury arc. It was thought therefore worthwhile to try the 2537 excitation. The experiment was made with a suitable crystal of colourless synthetic alumina and an exposure of 2 days was given with unexpected but very interesting results. On stopping the exposure, it was found that the alumina had been rendered phosphorescent and continued to emit a green radiation for a very long time afterwards. The crystal which was transparent to the 2537 radiations before the exposure was found to have become practically opaque.

Witherite ($BaCO_3$). See Table II

Witherite which is a crystalline form of barium carbonate has not been previously investigated for the Raman effect. The crystal is orthorhombic,

its structure being exactly similar to that of aragonite. The mineral was available in the form of a lump with hardly any natural faces. A small transparent portion was selected for illumination and a clear Raman spectrum could be obtained in about 18 hours. In addition to 4 Raman frequencies representing the internal vibrations of the CO_3 ion, six low frequency shifts have also been recorded. Rasetti's results for aragonite are given for comparison with those of witherite in Table II. The Raman frequency in witherite corresponding to the weak 852 line in aragonite has not been recorded, but a shift of 1511 which is probably a combination of it with 699 has been obtained.

It will be noticed that the frequencies for witherite are in each case lower than those for aragonite. This effect is much more marked in the low frequency region where the differences are quite large. This suggests that these low frequencies involve movements of the Ba ion in addition o rotations or translations of the CO_3 groups, the lower frequencies being ascribable to the heavier mass of Ba.

Barite ($BaSO_4$). See Table III

Barite is anhydrous barium sulphate crystallising in the orthorhombic system. A piece of clear transparent barite with a natural c (001) face was cut and polished with its faces perpendicular to the axes of the optical ellipsoid. To get the Raman spectra in various orientations the light was allowed to fall normally to one of the faces and the scattered light was examined from another face normal to it. Three different spectra recorded in this way, are reproduced in the Plate, the results being shown in Table III. The low frequency lines listed are fewer than those observed by Rasetti, evidently owing to the smaller dispersion of the instrument and consequent lack of resolution. The doublet at 450 and 462 for the sulphate ion has also not been resolved for the same reason. The intensities of the Raman lines appearing in the three different spectra are not comparable, as neither the exposure times nor the illuminated volumes were identical. The relative intensities of the different lines in the individual spectra are however seen to be clearly dependent on the orientation of the crystal. This is exhibited by the figures for estimated intensities given in Table III. Particularly interesting is the behaviour of the 76 and 187 lines which vary in intensity in a reciprocal fashion. It will be seen from the table that there are 8 frequencies recorded for the internal vibrations of the SO_4 ion instead of the 4 expected for a tetrahedrally symmetric ion oscillating in force-free space. The four components of highest frequency show marked variations of relative intensity with orientation. This is in agreement

with the results reported earlier by Balakrishnan, but the latter's conclusions are not all supported by the present investigation. A weak band ranging from 1198 to 1300 wave numbers is noticed here for the first time. Its intensity appears to vary markedly with the orientation of the crystal.

Celestite ($SrSO_4$). See Table IV

Celestite is anhydrous strontium sulphate crystallising in the orthorhombic system and is similar to barite in structure. The mineral was available in the form of an irregular piece. It was not therefore possible to orient the crystal in a known way, and hence a clear portion was illuminated in an unspecified direction. A clear picture could be obtained in about 30 hours. Four low frequency lines and eight frequencies of internal vibration of the SO_4 ion have been recorded. The Raman spectrum of celestite has been previously observed by Nisi and Krishnamurti, but it is clear from the present investigation that their results were incomplete. As is to be expected, the SO_4 frequencies for celestite are arranged on the same general scheme as for barite but are uniformly higher. There is a suspicion of a weak band in the same region as in the case of barite, but the spectra are not sufficiently intense to show it up clearly.

Gypsum ($CaSO_4\ 2H_2O$). See Table V

Gypsum is dihydrated calcium sulphate crystallising in the monoclinic system. The Raman spectrum of gypsum has been studied by a number of investigators. In the present investigation, a clear piece of gypsum cut with its faces perpendicular to the axes of the optical ellipsoid in the crystal was illuminated in three different orientations with the incident light normal to one of the faces, the scattered light being received through one of the other faces at right angles to it. The spectra are reproduced in the plate accompanying the paper.

The number of Raman lines of low frequency shift observed here is smaller than those observed by Rasetti due to the smaller dispersion of the instrument used and the consequent lack of resolution. A new feature noticed in the present work is that the line with 180 wave-number shift shows a marked change of intensity with orientation. Saxena has collated the results of various authors on the Raman shifts. His results are the most complete so far as the frequencies of the SO_4 ion are concerned. All the frequencies of the SO_4 ion in gypsum excepting the doubtful line recorded by Saxena at 1065 wave numbers have been observed by the present author. In addition a weak line at 1622 wave numbers and a weak band at 2249 have also been observed. Both the strong water bands which have

been reported by previous workers in gypsum have been observed at 3410 and 3480 wave numbers and their variation in intensity with orientation is also verified. A new fact which is observed with regard to these bands is that in a particular orientation the weaker of these bands has fainter components near it. Thus when 3410 is weaker, components are seen at 3244 and 3309 wave numbers, while when 3480 is weaker, there is a weak component at 3594 wave numbers. The band at 3240 has been previously reported by Krishnan.

It is seen from the tables that the SO_4 frequencies are grouped alike in the orthorhombic crystals barite and celestite but quite differently in the monoclinic crystal gypsum. The ν_4 frequency splits into the doublet 1115 and 1135 in gypsum, the higher frequency being much the more intense. In barite and celestite, on the other hand, it splits into 4 components in which the third in order of frequency is the most intense. The ν_3 frequency breaks into three components in gypsum with a wide separation, but it splits into only two components in barite and celestite, these having a smaller separation.

Tables

The numbers in the following tables indicate the wave-number shifts of the various Raman lines observed with the particular crystal mentioned at the head of the table. The numbers in brackets indicate a visual estimate of the intensity of the Raman lines referring to the strongest line of the particular plate as maximum. The orientation of the crystal is mentioned at the head of the table where it is known. α, β and γ refer to the directions of the axes of the optical ellipsoid in the crystal. OX and OY refer to the directions of illumination and observation respectively and OZ refers to a direction perpendicular to both. In some cases a Raman line falls exactly on top of a mercury line but it can then easily be observed in anti-Stokes excitation. The frequency shifts corresponding to such Raman lines have been marked with a star.

TABLE I

Quartz (SiO_2)

Illumination perpendicular to one of the hexagonal faces
Observation along the hexagonal axis

Wave-number shifts	129	140	208	267	359	399	466	508	696	808	886	901	931	940	1082	1162	1227
Intensity ..	(12)	(0)	(10)	(5)	(4)	(3)	(30)	(0)	(2)	(3)	(0)	(0)	(0)	(0)	(2)	(3)	(1)

References :—Saxena .. *Proc. Ind. Acad. Sci.*, 1940, **12**, 93.
Earlier literature will be found fully quoted in this paper.

TABLE II

Witherite ($BaCO_3$)

Setting of the crystal unknown

Crystal	Low frequency shifts						Frequencies of the CO_3 ion				
Witherite ..	54	85	135	164	186	221	699		1066	1416	1511
(Author) ..	(3)	(3)	(10)	(10)	(3)	(5)	(4)		(12)	(2) *d*	(1)
Aragonite ..	113	155	180·2	207·1	246·9	261·9	703·9	852·4	1084·9	1460·2	
(Rasetti) ..	(2)	(10)	(2)	(5)	(1)	(1)	(2)	(1)	(20)	(2)	

TABLE III

Barite ($BaSO_4$)

Directions of illumination and observation as shown in the table

β Axis along	α Axis along	γ Axis along	Low frequency shifts						Frequencies of the SO_4 ion								
			60	76	89	129	148	187	456	628*	645*	989	1088	1098	1142	1165	1198–1300 band
OY	OX	OZ		(6)	(8)	(5)	(6)	(9)	(16)			(20)	(5)	(2)	(15)	(6)	(1)
OY	OZ	OX	(2)	(15)	(3)	(2)	(2)	(5)	(16)			(20)	(3)	(5)	(10)	(7)	(0)
OZ	OX	OY		(15)	(3)	(4)	(5)	(6)	(16)			(20)	(6)	(3)	(9)	(7)	

References :—1. Nisi .. *Jap. Jour. Phys.*, 1930, **7**, 1.
2. Rasetti .. *Nuovo Cimento*, 1932, **92**, 72.
3. Krishnamurti .. *Ind. Jour. Phys.*, 1934, **9**, 303.
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4. Balakrishna .. *Proc. Ind. Acad. Sci.*, 1941, **14**, 257.

TABLE IV

Celestite ($SrSO_4$)

Setting of the crystal unknown

	Low frequency shifts					Frequencies of the SO_4 ion						
Celestite ..	63 (4)	92 (2)	122 (2)	189 (3)	460 (8)	623*	657 (2)	999*	1097 (2)	1112 (2)	1146 (5)	1180 (2)

References :—1. Krishnamurti .. *Ind. Jour. Phys.*, 1930, **5**, 181.
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TABLE V

Gypsum ($CaSO_4\ 2H_2O$)

Directions of observation and illumination as shown in the table

α Axis along	β Axis along	γ Axis along	Low frequency shifts						SO_4 frequencies and water bands													
			56	101	145	180	210	318	416*	492	588	620*	672	1004*	1115	1135	1162	2249	3244	3309	3410	3480	3584
OX	OZ	OY		(2)	(4)	(8)	(3)	(1)	Strong	(6)	(1)		(8)	Very Strong	(0)	(10)	(2)	(1)	(0)	(0)	(8)	(20)	
OZ	OX	OY	(3)	(4)	(4)	(3)	(2)	(1)		(6)	(1)		(8)		(0)	(10)	(1)	(0)			(16)	(6)	(0)
OY	OX	OZ	(3)	(2)	(2)	(5)	(2)	(1)		(6)	(0)		(8)		(0)	(10)					(8)	(4)	

References :—1. Krishnamurti .. *Ind. Jour. Phys.*, 1930, **5**, 180.
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The author is extremely grateful to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind encouragement and guidance throughout the progress of the work. The author is also thankful to Messrs. T. M. K. Nedungadi and P. G. N. Nayar for their help and advice during the progress of the work.

4. *Summary*

The paper reports the results of a study of the Raman spectra in various single crystals, the 2537 resonance radiations of a water cooled quartz mercury arc being used for excitation. The method enables quite small crystals to be employed. Quartz, barite, celestite, gypsum and witherite have been studied. Witherite has been examined for the first time, while the results obtained for celestite are much more complete than in any previous work. Other new results are the following :—

Quartz.—A group of four weak lines at 886, 901, 931 and 940 wave numbers has been observed which are probably overtones and combinations of fundamental frequencies.

Barite.—The low frequency lines at 76 and 187, as also the components at 1088 and 1098 of the ν_4 oscillation of the SO_4 ion show striking variations of intensity with orientation. A new faint band is noticed between 1198 and 1300 wave numbers.

Gypsum.—The low frequency line at 180 wave numbers shows a striking variation of intensity with orientation. A new line at 1622 and a weak band at 2249 have also been observed. The water bands at 3410 and 3480 have weak companions at 3244, 3309, and 3584 respectively in different orientations.

Alumina.—An attempt to excite the Raman spectrum of synthetic alumina with the 2537 radiation resulted in the crystal becoming strongly phosphorescent.

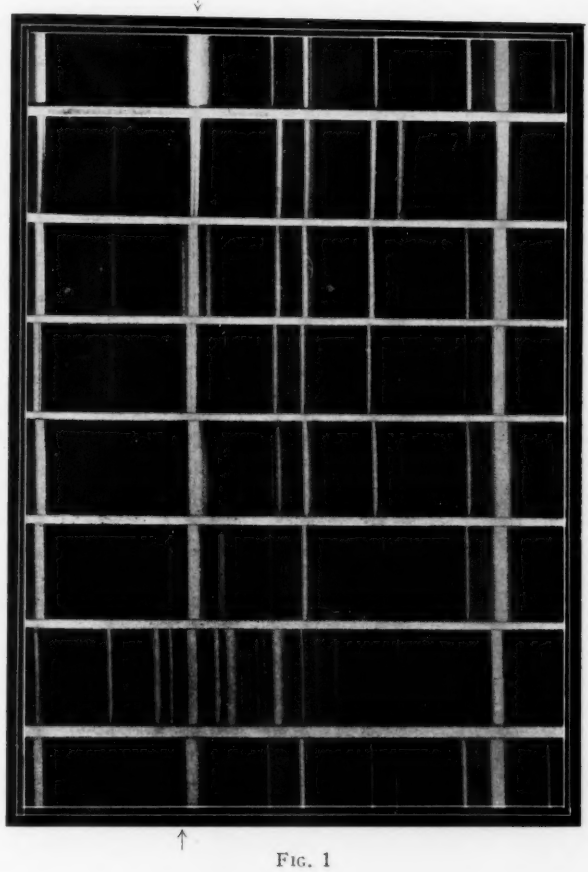

FIG. 1

Raman spectra of crystals

FIG. 2

Raman spectra of gypsum

EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part II. Crystals (*Contd.*)

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Received February 18, 1942

(Communicated by Prof. S. Bhagavantam)

1. Introduction

In a previous communication[1] the author has studied the effect of temperature on the intensities of Raman lines in some typical crystals like quartz, mercuric chloride and sodium nitrate. The frequencies chosen for study in those three cases are 465 cm.$^{-1}$, 315 cm.$^{-1}$, and 1065 cm.$^{-1}$, respectively. It has been observed that while according to Placzek's theory the intensities should increase with temperature both for the Stokes and the anti-Stokes lines, experimental results show that there is a marked decrease in intensity for the Stokes lines with increase of temperature. The rate of decrease is almost the same for all the three cases even though the frequencies studied are distinctly different. It has also been observed that the rate at which the intensity increases in the case of the anti-Stokes lines is not in conformity with that expected on the basis of Placzek's theory. The ratio of intensities between the Stokes and the anti-Stokes lines is, however, in agreement with the expected result.

From the study made by the author in those three cases, two important questions arise, namely, what will be the effect of temperature on different Raman frequencies in the same crystal and will there be any difference between the rate of variation of the intensities for the internal and for the lattice lines. Ornstein and Went[2] studied the effect of temperature on the different Raman lines in calcite and they concluded that the theoretical considerations of Placzek are applicable only for the proper frequencies of the crystal and not to the deformation frequencies very near the exciting line. Their results show no change in intensity for the 1085 line whereas the 710 line and the two lattice lines rapidly decrease in intensity with increase of temperature. This result is contrary to what has been obtained by the author in the case of the 1065 line in $NaNO_3$ which is quite similar to the 1085 line in calcite. In view of the discrepancies and with a view to get a coherent account of the effect of temperature on different Raman lines both internal and lattice in the same crystal and different crystals, the author is making a detailed study of this problem and this paper describes the results obtained in calcite.

2. *Experimental Arrangements*

The experimental arrangements are the same as those described in the previous communication. Light from a quartz mercury arc lamp condensed by a glass condenser is allowed to fall on one face of a nearly one-inch cube of calcite crystal and the scattered light emerging from one of the other faces is focussed on to the slit of a Fuess spectrograph. With an exposure of about 20 hours, intense and clear spectrograms have been obtained. The crystal is heated by means of a specially constructed electrical heater and a thermometer kept in contact with the crystal indicated the temperature with an accuracy of $\pm$ 5° C. Extreme care has been taken to see that the time of exposure and the intensity of the source are maintained constant while obtaining different spectra. The Raman spectra at various temperatures along with a set of intensity marks given by the method of varying slit-widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source are recorded on the same plate. The plate is run through a Moll micro-photometer and the intensities of the various Stokes and the anti-Stokes lines are computed in the usual way.

As the lines studied do not show any appreciable broadening in the temperature range employed, as can be seen from the Plate and also from the micro-photometric records which are not reproduced here, only the peak intensities have been compared.

3. *Results and Discussion*

The results given in the following tables are the mean of several observations. Table I contains the results relating to the effect of temperature on the intensities of the Stokes lines (155, 280, 710 and 1085) in calcite. The calculated results given in the table are obtained with the help of Placzek's relation quoted in Part I.

TABLE I

Temperature °K.	$\nu_j = 155$ cm.$^{-1}$			$\nu_j = 280$ cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·77	1·15	1·50	0·75	1·11	1·48
423	0·59	1·26	2·14	0·61	1·19	1·95
493	0·48	1·42	2·96	0·49	1·31	2·67

TABLE I—(*Contd.*)

Temperature °K	$\nu_j = 710$ cm.$^{-1}$			$\nu_j = 1085$ cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·81	1·04	1·28	0·86	1·01	1·17
423	0·66	1·06	1·60	0·72	1·02	1·42
493	0·58	1·11	1·91	0·62	1·04	1·68

In the above table, the ratio of the intensity of the Raman line at different temperatures to the intensity at 305° along with what is expected from the Placzek's theory are given. It is clear from the table that the quotient of the theoretical value by the value observed is much larger for the low frequency lines. This may be due to the fact that for low frequencies the elastic forces between the nuclei will be small. It is, therefore, evident that Placzek's theory in respect of the temperature dependence of the intensity of the vibrational Raman lines is not applicable for the vibrational Raman lines. The failure appears to be much more prominent in the case of lattice lines than for the internal oscillations in crystals.

Table II contains results relating to the effect of temperature on the anti-Stokes Raman lines ν_j being -155 and -280. The calculated results given in the table are obtained with the help of Placzek's relation already quoted in Part I.

TABLE II

Temperature °K.	$\nu_j = -155$ cm.$^{-1}$			$\nu_j = -280$ cm.$^{-1}$		
	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient	$\frac{I_T}{I_{305}}$ obs.	$\frac{I_T}{I_{305}}$ calc.	Quotient
305	1·00	1·00	1·00	1·00	1·00	1·00
373	0·91	1·31	1·44	0·92	1·40	1·52
423	0·85	1·54	1·81	0·85	1·70	2·00
493	0·78	1·86	2·38	0·80	2·16	2·70

It is clear from the above table that the intensities of the anti-Stokes lines decrease with temperature. In all cases previously studied by the author it has been observed that the anti-Stokes lines increase in intensity with temperature though not to the expected extent, but the present investigation

provides us with a new case where the intensities of the anti-Stokes lines also decrease with temperature. The discrepancy between the theoretical and the observed values is shown diagrammatically in Figs. 1 (*a*) and 1 (*b*).*

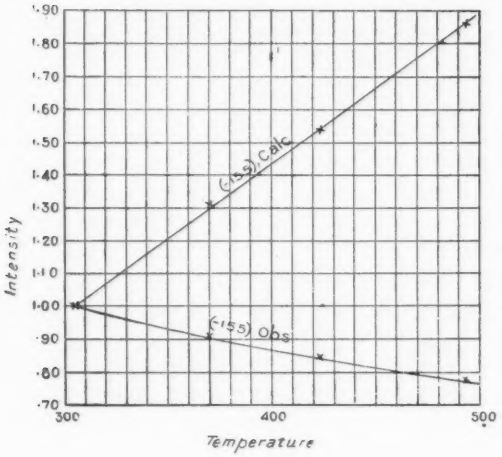


FIG. 1 (*a*)

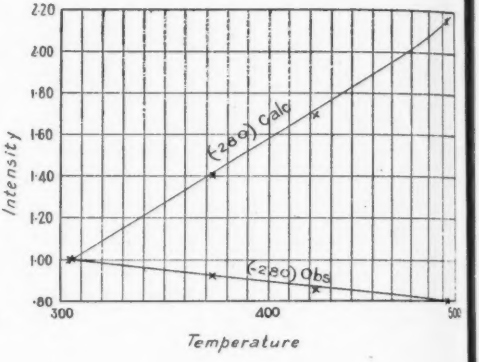


FIG. 1 (*b*)

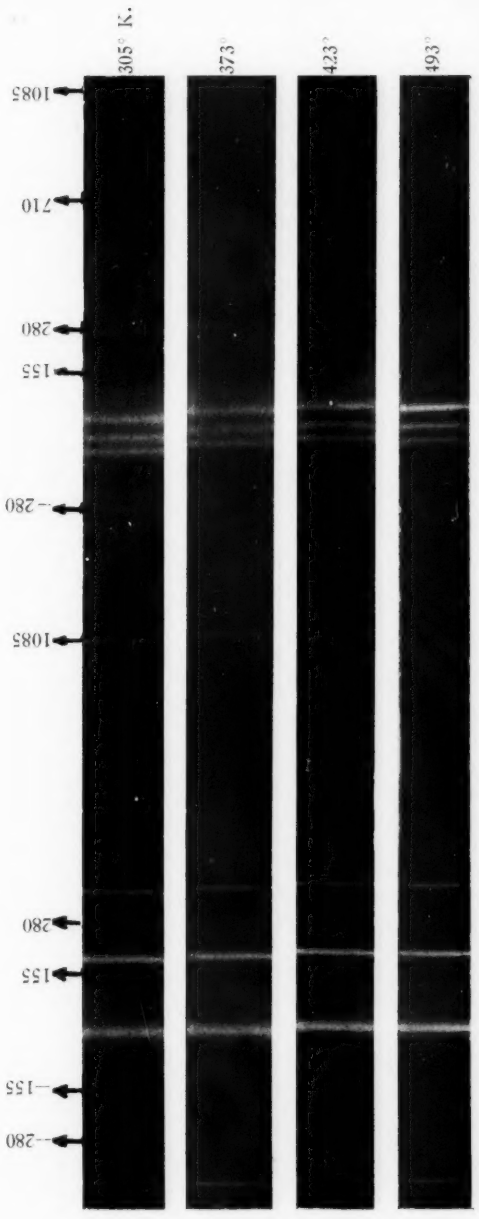
Table III contains results relating to the effect of temperature on the ratio of intensities of the Stokes and the anti-Stokes Raman lines.

TABLE III

Temperature °K.	$\nu_j = 155$ cm.$^{-1}$			$\nu_j = 280$ cm.$^{-1}$		
	$e^{\frac{h\nu_j}{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 . e^{\frac{h\nu_j}{kT}}$	$\frac{I_S}{I_{A.S.}}$ obs.	$e^{\frac{h\nu_j}{kT}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right) . e^{\frac{h\nu_j}{kT}}$	$\frac{I_S}{I_{A\ S.}}$ obs.
305	2·07	1·96	2·00	3·73	3·38	3·30
373	1·81	1·72	1·69	2·93	2·66	2·69
423	1·69	1·60	1·39	2·58	2·34	2·37
493	1·57	1·49	1·26	2·26	2·05	2·02

It can be seen from the above table that the ratio or the intensities of the Stokes and anti-Stokes lines agrees fairly well with the expected result at all temperatures.

* Diagrams showing the rate of fall for Stokes lines are not reproduced. As this is the first instance recorded where the intensity of the anti-Stokes lines also decreases with temperature, this diagram is reproduced with a view to bring out the discrepancy clearly.



Raman spectra of calcite at different temperatures

Table IV contains the results relating to the effect of temperature on the Raman frquencies or the positions of the Raman lines in calcite.

TABLE IV

Temperature °K.	Raman Frequencies			
305	156	282	708	1083
373	151	278	708	1083
423	148	272	710	1084
493	144	268	709	1083

It is obvious from the above table that the lines 710 and 1085 of calcite do not show any shifts whatsoever whereas the lines 155 and 280 show appreciable shifts towards the exciting lines between the temperature interval studied. These results are in agreement with the earlier observations of Ornstein and Went.

4. Summary

The effect of temperature on the intensities of Raman lines at 155, 280, 710 and 1085 cm.$^{-1}$ in calcite has been studied. It has been observed that for all the four lines, there is a decrease in intensity with increase of temperature but the rate of decrease is more rapid in the case of lattice lines than in the case of the internal lines. The intensities of the anti-Stokes lines (155, 280) also are found to be decreasing with increase of temperature but the ratio of the intensities of the Stokes and the anti-Stokes Raman lines at different temperatures is found to be in agreement with the expected result. It has been concluded that Placzek's theory regarding the dependence of the intensities of the vibrational Raman lines on temperature is not in agreement with experimental results. The disagreement is more prominent in the case of low frquency lines than in the case of high frequencies. It has also been observed that the two lattice lines in calcite exhibit a marked shift with increasing temperature towards the exciting line whereas the other lines remain in the same positions at different temperatures.

In conclusion, the author takes great pleasure in expressing his grateful thanks to Prof. S. Bhagavantam, HON. D.SC., Principal and Head of the Physics Department, under whose guidance the present investigation has been taken up.

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RAMAN EFFECT AND HYDROGEN BONDS

Part V. Mixtures of Acetic Acid with Ethers (Dioxan and Acetal)

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The Raman spectra of mixtures of acetic acid with a number of carbonyl compounds were reported in Part IV[1] and it was shown that anionoid solvents affect the molecular aggregation of acetic acid, though the breakdown of the ring dimers was not complete. The chief difficulty experienced in the above study was the interference from the carbonyl groups of the anionoid solvents with the result that only partial information could be obtained in each case. This may be contrasted with the use of water and phenol wherein all the three lines of acetic acid could be studied and complete information obtained. With a view to secure analogous conditions with anionoid solvents, types other than carbonyl compounds had to be examined. In this connection ethers as a group come in very handy and of these dioxan and acetal are the most convenient. Dioxan is a good solvent, has a conveniently high boiling point and has two anionoid oxygen atoms per molecule. In a similar way acetal is also good being the diethyl ether of the hypothetical acetaldehyde hydrate.

Though the Raman spectra of dioxan and acetal have been investigated in the past by a number of workers their usefulness as convenient solvents for the study of hydrogen bonds has been shown only by the present investigation. The spectra of these solvents purified by redistillation are given below:

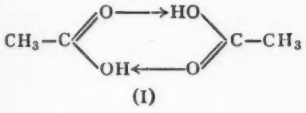
Dioxan.—180 (1) 435 (1) 483 (4) 837 (10) 850 (1) 1014 (6) 1107 (3) 1124 (1) 1214 (3) 1303 (6) 1332 (1) 1445 (8) 1459 (1) 2661 (0) 2719 (1) 2781 (1) 2858 (8*b*) 2889 (4) 2968 (9*b*).

Acetal.—350 (3) 450 (0) 530 (5) 660 (0) 810 (7) 850 (4) 919 (2) 1030 (3) 1063 (2) 1104 (4) 1150 (2) 1278 (4) 1340 (1) 1454 (10) 1486 (4) 2936 (5) 2982 (5).

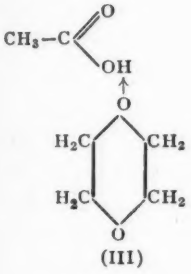
Mixtures of acetic acid with dioxan.—Spectra of mixtures of acetic acid and dioxan in three proportions 1 : 1, 1 : 2 and 1 : 4 were studied. With the first mixture it was found that the three C = O lines of acetic acid namely 1670,

1710 and 1745 cm.$^{-1}$ were of almost the same intensity. In the second mixture the 1670 cm.$^{-1}$ line was weakened to the point of extinction and the 1710 and 1745 cm.$^{-1}$ lines were fairly bright the latter being a little more intense than the former. In the third mixture containing 1 part of acetic acid and 4 of dioxan the 1670 cm.$^{-1}$ line had vanished completely and of the other two lines 1710 and 1745 cm.$^{-1}$ the latter was definetely brighter than the former. Thus progressive dilution with dioxan resulted in the disappearance of the first line and the brightening up of the other two of which the 1745 cm.$^{-1}$ line became stronger.

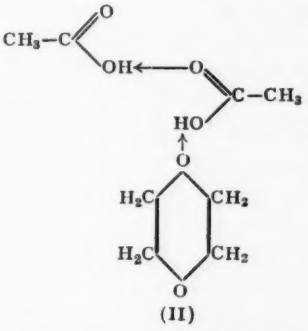
The above results are satisfactorily explained from the standpoint already described regarding the melecular aggregation of acetic acid. The anionoid oxygen of dioxan obviously attacks the hydroxylic hydrogen of the open dimers and the monomers forming complexes as represented below :



(I)



(III)



(II)

Of the three types of molecular aggregates (I), (II) and (III) the first contributes to the 1670 cm.$^{-1}$ line only since all the C=O groups are involved in H bonds of the ring type. Aggregate (II) should contribute equally to the two lines 1710 and 1745 cm.$^{-1}$ as there is one unco-ordinated C=O and one linearly co-ordinated C=O. On the other hand structure (III) should mean increase in intensity of the 1745 cm.$^{-1}$ line only since the C=O is unco-ordinated. In the 1 : 1 mixture since all the three lines are of the same intensity it may be concluded that (1) the breakdown of the ring dimers is only partial, (2) a considerable number of such molecules continue to exist, (3) aggregates of type II are mainly formed as a result of this mixture and (4) molecular aggregates of type III are probably not present

in any appreciable number. In the second mixture (1 : 2) most of the ring dimers should have been broken down since the 1670 cm.$^{-1}$ line has been considerably reduced in intensity. From the fact that the 1745 cm.$^{-1}$ line is the brighter of the other two it may be inferred that besides the predominance of aggregates of type II more of type III than before are formed. In the third mixture (1 : 4) the ring dimers have disappeared altogether and the mixture consists of types II and III only. The results are best explained even in the case of this dilute solution with the predominant occurrence of type II though the monomer aggregates (III) may be increasing with greater dilution.

It may be interesting to compare the results of the mixtures of acetic acid and water with those of acetic acid and dioxan. Though in both the cases the ring dimers are completely broken in dilute solutions, the fact that the 1670 cm.$^{-1}$ line fades almost to extinction in aqueous solution even in 1 : 1 proportion shows that there is in this case almost complete breakdown of the ring form at comparatively high concentrations. Thus water seems to be far more effective than dioxan. Another point of difference between these cases is that in water the only line present is 1710 cm.$^{-1}$ whereas in dioxan solution both 1710 cm.$^{-1}$ and 1745 cm.$^{-1}$ are present, the latter being the more intense of the two. This is due to the fact that in aqueous solutions the water molecules efficiently attack any unco-ordinated C = O bonds and reduce their frequency whereas in dioxan solutions such a possibility does not exist.

Mixture of acetic acid and acetal.—In the spectrum of the mixture (1 : 1) the 1670 cm.$^{-1}$ line was diminished in intensity and the other two lines became more intense (equal). Obviously the ether oxygen atoms of acetal serve the same purpose as those of dioxan. The results indicate that at moderate dilutions a considerable number of ring dimers break down to form aggregates of type II though this change is not so prominent as in the case of dioxan.

From the results obtained using mixtures of acetic acid with ethers and with carbonyl compounds it is definitely established that substances containing powerful anionoid centres such as C = O or $\diagup O \diagdown$ are capable of breaking down the molecular aggregates of acetic acid. It has already been shown that a powerful cationoid substance, phenol, has also considerable influence in regard to the above change. Hence the generalisation that both types of molecules can produce this effect, is quite valid. Water which possesses both the characteristics obviously acts in both capacities. This may account for the efficiency of water molecules in causing disruption of

ring dimers of acetic acid. It has been recorded that even in fairly concentrated aqueous solutions having limited amount of water the 1710 cm.$^{-1}$ line alone exists. Molecules which have only one type of active group are not so satisfactory. Besides its dual character water may have other advantages. It is quite possible that its small size also counts since difficulties due to steric factors will then be at a minimum.

In our attempts to explain the spectra of aqueous solutions of acetic acid three types of molecular aggregates were postulated. Of these the existence of ring dimers had already been independently established by other physical methods such as electron diffraction method. Strong support for the existence of the open type of dimers has now been obtained from the study of mixtures with other solvents, the most conclusive evidence being obtained with the following mixtures : coumarin-acetic acid, dioxan-acetic acid and acetal-acetic acid. The existence of monomers of acetic acid in association with the solvents to some extent is definitely brought out in the spectra of the dioxan-acetic acid mixture.

Summary

Raman spectra of mixtures of acetic acid with donor solvents not having C = O groups have been studied. The solvents chosen are dioxan and acetal. The results lend definite support to the mechanism described in previous papers (Parts III[2] and IV[1]) of the progressive breakdown of the ring dimers of the acid into associates of the open dimers and eventually of the monomers with the solvent molecules. The extraordinary efficiency of water in bringing about the breakdown is attributed to its dual capacity to act as both donor and acceptor.

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CHEMISTRY OF GOSSYPOL

Part I. Preparation and Properties

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Gossypol was first isolated as its acetic acid compound by Marchlewski[1] with great difficulty from the 'foots' of cotton-seed oil purification. Later Carruth[2] effected considerable simplification by employing raw cotton-seed kernels. They were first percolated with gasoline to remove most of the oil and subsequently extracted with ethyl ether in order to dissolve the gossypol. By the addition of glacial acetic acid to the concentrated ether extract and allowing to stand for several weeks crude 'gossypol acetate' was obtained. It was purified by crystallization from ether-glacial acetic acid mixture. From this product free gossypol was generated by dissolution in ether, treatment with water and subsequent distillation of the solvent. This method of isolation of gossypol has been adopted by all the subsequent workers, Clark,[3] Karrer and Töbler[4] and Adams *et al.*[5]

Another possible method of preparing gossypol from cotton-seed kernels suggests itself from the work of Carruth.[2] It consists in employing aniline in the place of acetic acid, thus producing the sparingly soluble anilino compound of gossypol. He found that gossypol itself was produced from this compound, when he decomposed it with alcoholic potash, removed the aniline formed by steam distillation and finally acidified the alkaline liquid by treatment with mineral acid. The scope of this procedure as a preparative method does not seem to have been explored by Carruth or by other workers.

In the course of his work, Carruth reported the existence of another form of gossypol in cotton-seed and he called it D-gossypol. It could not be extracted with ether with the same facility as ordinary gossypol and could be obtained by employing aniline as the solvent. At first it was thought to be a derivative of gossypol due to oxidation or hydrolysis. But Clark[6] showed that the aniline compound of D-gossypol was identical with that

of the ordinary gossypol and hence concluded that the greater difficulty in the isolation of this fraction was due to the existence of a portion of the gossypol content of the seeds in a combined form (bound gossypol). Later Halverson and Smith[7] showed that by moistening the oil-free seeds the extraction of gossypol with ether could be rendered complete. By employing seed powder moistened with 22% of water both free and bound gossypol could be isolated. In their experiments they obtained gossypol as the aniline compound and since it is sparingly soluble, quantitative comparisons could be readily effected by weighing it. Though no attempt has been made in the past to explain the nature of the bound gossypol it may be suggested at this stage that it is probably a combination with free fatty acids present in the seed. In support of this may be mentioned the marked tendency exhibited by gossypol to combine with fatty acids and ketones to form sparingly soluble compounds which undergo decomposition in the presence of water.

In the course of our attempts to work out a convenient method of preparing gossypol in fairly large quantities, the methods of Carruth were first employed. His acetic acid method gave a poor yield of gossypol-acetic acid and consequently led to a low recovery of gossypol. With a view to improve the yield moistening the meal had to be carried out. But then no gossypol-acetic acid would separate from the extract even after allowing to stand for a considerable length of time. This is due to the fact that its separation is markedly prevented by the existence of moisture and also of any residual oil. Consequently precipitation with aniline had to be employed. The formation of the aniline compound is not adversely affected by the presence of moisture. In the course of our trials it was found inconvenient and unnecessary to use such a large quantity of water as suggested by Halverson and Smith and 10% of moisture on the weight of the oil-free kernels was found to be the most convenient.

Again, the need for large quantities of petroleum ether for removing the oil and of ether for extracting gossypol from cotton-seeds made this preparation very costly. The loss of these volatile solvents was particularly large. The possibility, therefore, of using other solvents was explored. Alcohol, in spite of the high solubility of the substance in it, was found to be unsuitable. It gave rise to very poor yields and seemed to cause considerable decomposition of the colouring matter, especially when attempts were made to recover the solvent. On the other hand, chloroform was found to be quite satisfactory. There was no need for the preliminary removal of the oil or for moistening the seeds. Complete extraction was effected by cold percolation of the fresh seed meal for a comparatively short

period. The anilino compound separated out quite readily and a good portion of the solvent could be recovered without any reduction in the yield of gossypol. This solvent seems to be the most satisfactory for extraction.

Though the precipitation of gossypol as its aniline compound is quick and quantitative, the liberation of the colouring matter from it is not so simple as from gossypol-acetic acid. Carruth's method[2] of empolying alcoholic potash leads to considerable decomposition and the isolation of even a small yield of pure gossypol is very difficult. By the action of concentrated sulphuric acid Clark[6] and later Adams and co-workers[8] noted that the aniline compound gave rise to gossypol. The liberated gossypol was purified by conversion into the acetic acid compound and subsequent regeneration. Though this method works fairly satisfactorily when small quantities of the anil are employed, the yield is not very good with larger quantities. The reaction takes place in a complex manner, giving rise to various other products and thus considerably reducing the yield and purity of gossypol. A new method has, therefore, been worked out. This consists in heating the dry anilino compound with acetic anhydride for a few minutes in order to produce a clear soultion. When it is subsequently poured into ice water, crude gossypol-acetic acid is obtained in almost quantitative yield. The aqueous solution is found to contain acetanilide. Under these conditions no acetylation of gossypol takes place to any appreciable extent. As a matter of fact Adams *et al.* have recorded that no acetylation of gossypol is effected by acetic anhydride in the absence of a catalyst even when heated for half an hour. The above method has, therefore, been adopted largely for the preparation of gossypol.

The gossypol-acetic acid obtained by the hydrolysis of the anilino compound was found to be identical with the sample obtained by direct precipitation from the ether extract of the seeds. For its recrystallization it is essential to avoid heating in the presence of water since under this condition the product contains high carbon obviously due to partial decomposition of the compound into gossypol. In the cold it is not markedly affected by water but on boiling for a few minutes with it, complete conversion into gossypol takes place. A remarkable feature about our samples of gossypol is that they all have the same melting point (189° decomp.) irrespective of the solvent employed for the crystallization and they also appear more or less in the same crystalline form (yellow rectangular plates). It may be useful to recount here the previous records regarding crystalline appearance and melting point. Carruth,[2] Clark,[3] Karrer and Töbler[4] and Schmid and Margulies[10] reported the melting point of gossypol as 188°,

214°, 199° and 184° respectively. An explanation of this variation was offered by Adams *et al.*[5] who claimed to have obtained three definite crystalline forms of gossypol, each having a characteristic melting point, using different solvents for crystallization. When ether was employed the substance was a yellow micro-crystalline powder melting at 184°; from chloroform, it was obtained as bright yellow needles melting at 199° whereas from ligroin it was produced as small bright yellow plates melting at 214°. The interconversion of the forms could be effected by recrystallization using the appropriate solvent. It may, however, be pointed out that this does not exactly agree with the results of previous workers since Karrer and Töbler obtained a melting point of 199° for their sample crystallized from ether-petroleum ether mixture and not from chloroform, and Clark obtained a melting point of 214° for samples crystallized from dilute alcohol or from a mixture of ether and light petroleum. A scrutiny of the photomicrographs of Adams *et al.*[5] discloses that there is no correspondence between them and the description of the crystals given. The differences between the crystal structures do not seem to be fundamental. Our experience with a number of batches of gossypol preparations is not in accordance with the statements of Adams *et al.* All our samples were bright yellow in colour, had more or less the same crystalline form and the same melting point (189° decomp.). Methyl and ethyl alcohols and acetone were not suitable for getting good crystals since the substance was highly soluble in them. Ligroin, chloroform, benzene and ether-petroleum ether mixture were suitable and the products appeared very much like those presented in the photomicrographs of Adams *et al.* for samples obtained from chloroform.

Previous workers have stated that gossypol does not give correct results in combustion analysis and that it even gives an appreciably high methoxyl value (Clark[11]; Adams *et al.*[12]). Employing pure samples crystallized from chloroform, ether and ligroin, we have obtained consistent values for carbon and hydrogen agreeing with the formula $C_{30}H_{30}O_8$ and they do not give any methoxyl value when tested by the micro-Zeisel method. Our samples of gossypol were found to possess all the properties and exhibit all the colour reactions recorded in the literature. A few new observations are given in the experimental section.

Experimental

The seeds of the Cambodia cotton (*Gossypium hirsutum*) were the most suitable since analysis of different species indicated that these contain the largest amount of gossypol. Delinting of the seeds with concentrated sulphuric acid rendered the separation of kernels easy but this

treatment was not found to be convenient or quite necessary. Breaking up the raw seeds in a disintegrator and sieving yielded the kernels in a satisfactorily powdered form and could be used directly. Fresh material was employed as far as possible since storage caused considerable deterioration in yield.

Extraction.—The method of Carruth was first adopted. The dry meats were first percolated with pertoleum ether in order to remove the oil and then with ethyl ether in order to extract the gossypol. When the concentrated extract was treated with glacial acetic acid and allowed to stand for 4 weeks, the yield of gossypol acetic acid was 0·12% of the kernels taken. This corresponds to a yield of 0·11% of gossypol. When, however, aniline was added in the place of acetic acid, the separation of the anil was complete in about 24 hours and the yield of the pure anil amounted to 0·3% corresponding to a yield of 0·22% of gossypol.

With a view to improve the extraction of gossypol the fat-free meal was impregnated with water as suggested by Halverson and Smith (*loc. cit.*). 10% of moisture was found to be convenient as more than this amount yielded a pasty mass difficult to handle and this did not increase the yield very much.

The seed meal (1 kg.) was percolated with petroleum ether in order to remove the oil and the fat-free residue, thoroughly mixed with 10% of water, was extracted with peroxide-free ether by cold percolation. When glacial acetic acid was added to the concentrated extract, the separation of gossypol-acetic acid did not take place to any extent in the course of one month. On the other hand, addition of excess of aniline gave a good yield of the anilino compound amounting to 0·8% of the weight of the raw seeds. This corresponded to a yield of about 0·6% of gossypol.

The preliminary removal of the oil is not absolutely essential for obtaining fairly good yields of the anilino compound though it may be said to be desirable. Nor is it essential to add ethylene glycol or pyridine to the ether extract in order to complete the precipitation of the anil as suggested by Halverson and Smith.

The fresh meal (1 kg.) ground to pass through a 10-mesh sieve was treated with 100 c.c. of water and thoroughly mixed. It was extracted by cold percolation six times with peroxide-free ether containing 3% of alcohol and 2% of water in the course of 72 hours. The combined ether extracts were filtered, if necessary, treated with 10 c.c. of aniline and the solvent distilled off as far as possible. On adding sufficient petroleum ether to dissolve the oily matter and allowing to stand overnight, a good yield of

bright yellow anilino compound was obtained. After filtering the solid the mother-liquor was treated with a little more aniline to make sure that the precipitation was complete. The yield frequently amounted to 0·75%.

When employing chloroform fresh cotton-seed meal (1 kg.) was directly extracted with it by cold percolation (4 times) in the course of 12 hours. The combined extracts were treated with aniline as before and the solution concentrated by distilling off the solvent. Further operations were just as given above and the yield of the anilino compound was 0·8%.

Hot extraction of the seeds always resulted in poor yields.

Decomposition of the anilino compound to obtain gossypol.—the anilino compound obtained as described above was purified by crystallization first from aniline and again from hot benzene. It was thus obtained as an orange yellow crystalline solid (rectangular plates) melting with decomposition at 303°. It was insoluble in most of the solvents and also in dilute acids and alkalis and was unaffected by boiling with glacial acetic acid for several hours. It was however, easily soluble in alcoholic potash, producing an orange red solution and undergoing slow decomposition.

The method of Carruth using alcoholic potash gave rise only to a very small yield of impure gossypol (0·2 g. from 2 g. of the anil) which was very difficult to purify. Treatment with concentrated sulphuric acid according to the procedure of Clark at 90° for 5 minutes gave better results when small quantities of the anil were employed. The crude gossypol obtained by pouring the sulphuric acid soultion in ice water was converted into the acetic acid compound and recrystallized. Though the yield was good (0·6 g. from 1 gram of the anil) and the melting point (184°) satisfactory the sample was rather brown and the colour was difficult to remove by repeated recrystallization from ether-petroleum ether mixture. When the experiment was repeated with larger quantities of the anil (10 g.), the yield of gossypol-acetic acid was very small, the main product being a highly coloured (pink red) substance which did not melt below 340°. It was found to contain some nitrogen and sulphur also. All attempts to obtain gossypol or any of its derivatives by further treatment failed.

The most satisfactory method using acetic anhydride was carried out as below:—

The anil (5 g.) was treated with acetic anhydride (25 c.c.) and the mixture heated on a wire-gauze till a clear solution was obtained. After cooling it was poured into ice water. The product first separated as a liquid and when subjected to vigorous stirring, turned into a yellow solid. It was filtered

and washed with hot water. It was subsequently dissolved in glacial acetic acid by warming and the cold solution treated with water. By this treatment gossypol-acetic acid was obtained as a bright yellow crystalline substance melting at 185° with decomposition. The yield was about 4 g. The aqueous mother-liquor from which the crude product separated yielded acetanilide on concentration.

The sample of gossypol-acetic acid had all the properties mentioned in the literature. It gave no tests for nitrogen and yielded acetic acid vapours on heating and after a final recrystallisation from acetic acid petroleum ether or ether-petroleum ether, yielded correct results by combustion analysis. [Found : C, 66·3 ; H, 5·9 ; $C_{30}H_{30}O_8$, CH_3COOH requires : C, 66·4 ; H, 5·9%.]

Care should be taken not to precipitate the acetic acid compound by the addition of water to a hot solution in acetic acid since this brings about partial decomposition into gossypol. Though the product gives nearly the same melting point and exhibits other properties similar to pure gossypol-acetic acid, its carbon value is markedly high indicating admixture with gossypol.

Preparation of gossypol.— The decomposition of gossypol-acetic acid was carried out by previous workers by dissolving it in ether, adding water to the solution and distilling off the ether. Gossypol separated out in the form of crusts. It has now been found that this could be effected by boiling gossypol-acetic acid with water for 15 minutes. The solid was filtered, dried (1 g.) and dissolved in the minimum quantity of peroxide-free ether (10 c.c.). The clear solution was then treated with excess of petroleum ether. Gossypol crystallised out slowly as yellow rectangular plates, melting at 189° with decomposition. In a similar way it could also be crystallised by dissolving in chloroform and adding petroleum ether. This sample also melted at the same temperature and had the same crystal form [Found : C, 69·3 ; H, 5·9 ; $C_{30}H_{30}O_8$ requires : C, 69·4 ; H, 5·8%].

The pure substance is tasteless and odourless. It gives no methoxyl value when tested by micro-Zeisel and readily forms the anilino and acetic acid derivatives.

The following reactions of gossypol have been noted besides those already described by previous workers. It reduces Fehlings solution and ammoniacal silver nitrate rapidly. It is quite stable in the presence of cold hydrochloric and sulphuric acids, dilute or concentrated, but it is readily changed by nitric acid and sodium peroxide. It does not give the typical colour reactions of flavones forming pyrylium salts when subjected

to reduction in acid or alkaline medium. Though it contains large number of phenolic hydroxyl groups, it does not readily react with phenyl isocyanate in benzene solution. It does not combine with picric acid to form a picrate. In alkali it produces a pale yellow solution and no characteristic differences are noticed with alkaline buffer solutions with different p_H.

Summary

Various methods of extracting gossypol from cotton-seed meal have been examined: (1) removal of the oil with petroleum ether and then extraction of gossypol with ether, (2) same as (1) but moistening the seed meal before ether extraction, (3) precipitation of gossypol as the acetic acid compound, (4) precipitation of gossypol as the aniline compound and (5) use of other solvents particularly chloroform not so far investigated. It has been confirmed that moistening of the meal is necessary for complete extraction with ether and when this is done only aniline works satisfactorily as the precipitant. The preliminary removal of the oil is not absolutely essential though desirable. With chloroform as the solvent, neither removal of the oil nor addition of moisture is necessary. Hence the use of chloroform as the solvent and aniline as the precipitant is most satisfactory. For recovering gossypol from the anilino compound decomposition using potash and sulphuric acid are not satisfactory. A new method has been evolved using acetic anhyride. Pure gossypol thus obtained melts at 189° and the solvent employed makes no difference. It gives no methoxyl values. A few other properties are described.

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STUDIES ON THE DEPENDENCE OF OPTICAL ROTATORY POWER ON CHEMICAL CONSTITUTION

Part XX. Stereoisomeric Xylidinomethylenecamphors

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In the present communication we give an account of our experiments on the optical rotatory dispersion of the condensation products of oxymethylenecamphors (*d*, *l*, *dl*) with *m*-xylidines (1 : 3 : 5 and 1 : 3 : 4) and *p*-xylidine (1 : 4 : 5).

The condensation product of oxymethylene-*d*-camphor with 1 : 3 : 4-xylidine was an oil which refused to solidify.

TABLE A

$[\alpha]^{35^\circ}_{Hg5461}$

Compound	MeOH	EtOH	Acetone	Pyridine	Chloroform	Benzene
I. *R·NH-C$_6$H$_4$	480·0° (86·78)	451·3° (81·83)	448·9° (83·08)	433·2° (81·21)	424·6° (78·57)	367·1° (70·71)
II. *R·NH-C$_6$H$_3$(CH$_3$)	454·4 (85·21)	439·9 (81·02)	442·3 (82·31)	405·8 (80·48)	384·8 (68·55)	352·6 (71·37)
III. *R·NH-C$_6$H$_3$(CH$_3$)	465·0 (79·56)	440·8 (80·13)	425·8 (78·77)	401·6 (74·15)	401·6 (74·15)	355·4 (66·65)
IV. R·NH-C$_6$H$_3$(CH$_3$)$_2$	429·5 (72·29)	407·7 (70·66)	383·2 (71·73)	377·2 (64·71)	370·5 (67·95)	329·9 (62·37)
V. R·NH-C$_6$H$_3$(CH$_3$)$_2$	415·3 (66·27)	403·5 (64·11)	408·8 (65·69)	408·1 (65·51)	400·0 (63·61)	368·2 (59·44)

Figures within brackets refer to values of K of the Drude equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$, for λ, when $\lambda = \sqrt{\lambda_0^2 + 1}$, and are called the ' absolute rotations '.*

* Singh, Bhaduri and Barat, *J. Ind. Chem. Soc.*, 1931, **8**, 345. R = C_8H_{14}

The Effect of Chemical Constitution and the Nature of Solvent on Rotatory Power.—The analogy between the effect of substitution on optical activity and on other electrophysical properties, such as specific inductive capacity, electro-magnetic rotation, and dissociation constant of substituted acids and bases, has been experimentally confirmed by various workers.[1] It is further confirmed by the present data given in Table A :—on comparing the rotatory powers of anilinomethylenecamphor (I) and *m*- and *p*-toluidinomethylenecamphors (II and III), it is found that the effect of the introduction of a methyl group is to lower the rotation of the parent compound (I). It was anticipated that the introduction of a second methyl group, as in xylidinomethylenecamphors (IV and V), would lower the rotation of the parent compound (II), owing to the *polar* effect of the first methyl group being reinforced by that of the second like group. This is clearly borne out by the rotatory power data of *m*-toluidinomethylene camphor (II) and *m*-xylidinomethylenecamphor (IV). The same is the case with *m*-toluidinomethylene camphor (II) and *p*-xylidinomethylenecamphor (V), except that in pyridine, chloroform and benzene *p*-xylidinomethylenecamphor gives higher values of rotatory power, which militates against the above-mentioned generalisation based on the *polarity* of substituent groups. It is thus clear that the *polar* effects of groups may be modified by the nature of the solvent.

The sequence of decreasing rotatory power of the substituent groups in these compounds is $H > CH_3 > (CH_3)_2$. This agrees exactly with the specific inductive capacity of the bases, *viz.*, aniline, toluidines, and xylidines, and also with the dissociation constants of the same bases except that the order is reversed in the latter case.

In the Drude's equation, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$, when $\lambda^2 = \lambda_0^2 + 1$, *i.e.*, for the value of λ always in the infra-red region beyond 10,000 A.U., K_0 is *numerically* equal to the specific rotation $[\alpha_0]$, the ' absolute rotation ' of the compound. This value of K_0 is independent of the wavelength and for reasons already stated in a previous communication,[2] instead of confining the comparison to a single wavelength which may lead to quite incorrect conclusions, we should take into account the different numerical values of K_0 of the different compounds in a particular solvent. From such a study (see Table A) we have, subject to minor variations, arrived at conclusions similar to those stated in the preceding paragraphs.

The compounds studied in the present paper, like other condensation products of aromatic bases with oxymethylenecamphor (Singh and Bhaduri,

loc. cit.), are without exception, found to obey the simple dispersion equation, of Drude, $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$, (Tables I & II).

It is found that the order of decreasing rotatory power in different solvents is methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene (Tables I & II). The sequence of the dielectric constants of the solvents is also the same.

Physical Identity of Isomers.—The values of rotatory power of *d*- and *l*-forms in different solvents (Tables I & II) are identical within limits of experimental error. Out of 96 observations now recorded, in as many as 87 cases the difference in the numerical value of the specific rotatory power of the opposite isomers corresponds to a difference of less than 0·01° in the observed angle of rotation and in the remaining cases the angle lies between 0·01° and 0·02° which is the limit of experimental error allowable in such measurements. This further supports Pasteur's principle of molecular dissymmetry, according to which the two forms, *dextro* and *lævo* must possess equal and opposite rotatory power.

Examples of *racemic* forms having identical melting points with those of the active forms are very rare. A few examples have already been referred to in previous communications.[3] In the present paper, we record one more instance, *viz.*, (1 : 3 : 5)-*xylidinomethylenecamphor*, m.p. 165°–167°.

Experimental

General Method of Preparation.—The solution of the free base (1 mol. proportion) in glacial acetic acid is added to a solution of oxymethylene-*d*-camphor (1 mol. proportion) in methyl alcohol, when a precipitate usually separates at once ; if not, it is diluted with water ; in case any oil separates, it is left overnight when it usually solidifies. It is then crystallised out of dilute methyl alcohol.

The *lævo* and the *racemic* compounds described in the present paper were prepared in the same way as the corresponding *dextro* isomers and have the same crystalline form and similar solubility.

s-m or 1 : 3 : 5-*Xylidinomethylene*-d-*camphor*, white prismatic needles, m.p. 165°–67°. [Found : C, 80. 37 ; H, 8. 93 ; and N, 5·04. $C_{19}H_{25}ON$ requires C, 80·56 ; H, 8·83 and N, 4·95 per cent.] It is fairly easily soluble in all the ordinary organic media. The *l*-form, m.p. 165°–67°. [Found: N, 4.98 per cent.] The *dl*-form, m.p. 165°-67°. [Found : N, 5·07 per cent.]

The condensation product of oxymethylene-*d*-camphor with 1 : 3 : 4-xylidine was an oil which refused to solidify.

TABLE I

s-m-Xylidinomethylenecamphors (*Formula IV, Table A*)

Solvent :		Methyl alcohol		Ethyl alcohol		Benzene		Pyridine		Acetone		Chloroform	
Concentration g./100 c.c.	*d*	0·4028		0·4024		0·4032		0·4044		0·4020		0·4076	
	l	0·4000		0·4060		0·4000		0·4020		0·4052		0·4000	
Calculated	$\frac{[\alpha]}{\lambda_0}$	$\pm \frac{72\cdot29}{\lambda^2-0\cdot1300} + 0\cdot3606$		$\pm \frac{70\cdot66}{\lambda^2-0\cdot1249} + 0\cdot3534$		$\pm \frac{62\cdot37}{\lambda^2-0\cdot1086} + 0\cdot3295$		$\pm \frac{64\cdot71}{\lambda^2-0\cdot1271} + 0\cdot3565$		$\pm \frac{71\cdot73}{\lambda^2-0\cdot1115} + 0\cdot3339$		$\pm \frac{67\cdot95}{\lambda^2-0\cdot1153} + 0\cdot3396$	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5086}	..	+561·2°	−562·5°	+528·1°	−528·4°	+415·8°	−415·0°	+492·1°	−491·4°	+487·6°	−486·3°	+473·6°	−475·0°
Ag_{5209}	..	512·6	511·3	483·3	481·6	383·2	383·8	447·7	449·0	449·1	449·2	435·6	435·0
Hg_{5461}	..	429·5	430·0	407·7	407·7	329·9	328·8	377·2	378·1	383·2	383·8	370·5	371·3
Hg_{5770}	..	355·0	353·8	338·1	337·5	276·4	276·3	312·8	312·2	322·2	322·0	310·5	310·0
Na_{5893}	..	332·7	332·5	316·9	317·8	261·6	261·3	294·3	293·6	304·6	304·8	293·2	293·8
Li_{6141}	..	299·1	298·8	285·8	285·8	235·7	236·3	263·4	263·7	276·1	274·0	265·0	263·8
Cd_{6438}	..	253·2	253·8	243·6	243·9	204·6	203·8	225·1	225·2	237·6	236·9	227·1	226·3
Li_{6703}	..	225·7	226·3	217·5	218·0	183·5	183·8	200·4	200·2	211·6	212·2	202·5	203·8
		Solution exhibited mutarotation : $[\alpha]_{Hg5461}$ = 429·5° → 422·0° in 20 hours		No mutarotation				Solution exhibited mutarotation : $[\alpha]_{Hg5461}$ = 377·2° → 369·7° in 20 hours		Solution exhibited mutarotation : $[\alpha]_{Hg5461}$ = 383·2° → 367·0° in 24 hours		Solution exhibited mutarotation : $[\alpha]_{Hg5461}$ = 370·5° → 360·5° in 20 hours	

TABLE II

p-Xylidinomethylenecamphors (*Formula V, Table A*)

Solvent :		Methyl alcohol		Ethyl alcohol		Benzene		Pyridine		Acetone		Chloroform	
Concentration g./100 c.c.	*d*	0·4044		0·4016		0·4060		0·4056		0·4012		0·4012	
	l	0·4008		0·4060		0·4020		0·4000		0·4052		0·4040	
Calculated	$\frac{[\alpha]}{\lambda_0}$	$\pm \frac{66\cdot27}{\lambda^2-0\cdot1388} - 0\cdot3762$		$\pm \frac{64\cdot11}{\lambda^2-0\cdot1395} - 0\cdot3735$		$\pm \frac{59\cdot44}{\lambda^2-0\cdot1364} - 0\cdot3693$		$\pm \frac{65\cdot51}{\lambda^2-0\cdot1381} - 0\cdot3716$		$\pm \frac{65\cdot69}{\lambda^2-0\cdot1375} - 0\cdot3708$		$\pm \frac{63\cdot61}{\lambda^2-0\cdot1386} - 0\cdot3723$	
Line		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]		Obs. [α]	
		d	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*	*d*	*l*
Cd_{5086}	..	+552·6°	−553·9°	+537·9°	−537·0°	+485·3°	−486·4°	+543·6°	−542·5°	+542·1°	−541·8°	+529·7°	−528·5°
Ag_{5209}	..	500·7	500·2	486·9	486·5	442·0	440·6	492·9	491·3	492·2	490·0	479·8	479·0
Hg_{5461}	..	415·3	415·3	403·5	402·8	368·2	367·0	408·1	410·0	408·8	409·6	400·0	398·6
Hg_{5770}	..	338·8	339·3	329·3	330·1	299·4	300·1	333·0	333·8	334·0	334·4	325·2	325·5
Na_{5893}	..	317·7	318·0	308·8	308·0	280·4	281·0	313·1	313·8	312·8	312·2	304·0	305·6
Li_{6104}	..	284·3	283·2	275·2	274·7	252·5	252·5	280·3	278·8	279·2	280·0	271·7	271·0
Cd_{6438}	..	239·8	240·7	232·8	232·8	213·1	213·9	236·7	237·5	238·1	238·2	230·6	230·2
Li_{6703}	..	213·9	212·1	206·7	206·9	189·7	189·1	210·7	210·0	210·6	209·8	204·4	204·2
		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation		No mutarotation	

p- or 1 : 4 : 5-*Xylidinomethylene*-d-*camphor*, shining white long rectangular plates or needles, m.p. 123°-24°. [Found : C, 80·43 ; H, 8·85; $C_{19}H_{25}ON$ requires C, 80·56 ; H, 8·83 and N, 4·95 per cent.] It is freely soluble in the ordinary organic media. The *l*-form, m.p. 123°-24°. [Found : N, 5·16 per cent.] The *dl*-form, m.p. 101°. [Found : N, 5·04 per cent.]

The condensation of these bases with *d*-camphorquinone failed.

The rotatory power determinations were made in a 2-dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expreseed as μ or 10^{-4} cm.

A grateful acknowledgment is made to the Bihar Government for the grant of a Research Scholarship to one of us (B.B.), which enabled him to take part in this investigation.

Summary

1. The rotatory power of the *dextro*- and *lævo*- forms of xylidinomethylenecamphors (*m* and *p*) are identical, and obey the *simple* dispersion law of Drude.

2. The substitution of a methyl group for an atom of hydrogen in the phenyl group of anilinomethylenecamphor lowers its rotatory power. The introduction of a second methyl group as in the xylidinomethylenecamphors generally lowers the rotation still further, owing to the *polar* effect of the first methyl group being reinforced by that of the second like group.

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VISIBLE FLUORESCENCE AND CHEMICAL CONSTITUTION OF COMPOUNDS OF THE BENZO-PYRONE GROUP

Part III. Further Study of Structural Influences in Coumarins

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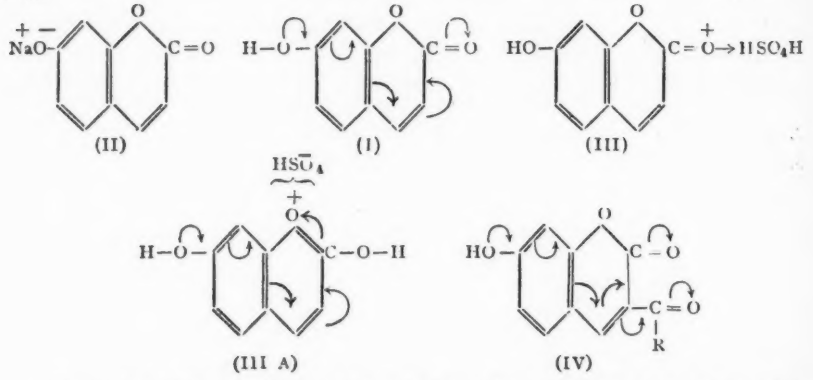
In two previous communications[1,2] which may be considered as Parts I and II of this series certain aspects of the subject have been discussed. In Part I a general study of hydroxy coumarins and hydroxy chromones was made and comparison effected. The subsequent part dealt with the remarkable influence of carbonyl groups in the 3-position of 7-hydroxy coumarins in enhancing fluorescence. In this connection it was pointed out that emission of fluorescence is accompanied by increasing capacity of the molecule to exhibit resonance. Formulæ I, II and III may represent the changes taking place in umbelliferone when dissolved in aqueous alkali and in concentrated sulphuric acid. The normal polarisation in umbelliferone (I) is increased by the formation of the negative ion in alkaline solutions and of the hydrogen bond in sulphuric acid. The formation of an oxonium salt (III A) is also possible and will produce a similar effect. The introduction of a carbonyl in the 3-position intensifies resonance as shown in IV and consequently the substances fluoresce strong even in neutral alcoholic solution.



A number of possibilities of verifying the validity of the above ideas and of amplifying existing knowledge suggest themselves. Several coumarin

compounds having the desirable structures have therefore been prepared and their fluorescence examined. The results are presented in the form of a table and based on them the following special points may be mentioned,

A. Effect of pyrone double bond

If the above explanations are valid the reduction of the pyrone double bond in umbelliferone should mean complete absence of fluorescence in the product as there should be no further possibility of resonance initiated by the carbonyl, reaching the hydroxyl across the molecule as in (I). Dihydro-umbelliferone and seven derivatives (V, R = H or C_6H_5, CH_2CO_2H, etc. and R′ = H or CH_3) have been prepared and studied. All of them exhibit no fluorescence in solutions in alcohol, in dilute alkali or in concentrated sulphuric acid. This forms an interesting support of the explanations given above.

B. Effect of cyano and phenyl groups in position 3

In continuation of the work relating to the influence of the carbonyl group in the 3-position, the effect of groups which are similar to it such as the cyano and the phenyl have now been studied. 3-cyano-umbelliferone (VI) and a few 3-phenyl-7-hydroxy-coumarins (VII) have been prepared and examined. Observations regarding their fluorescence are given in the Table and from them it appears that the cyano and phenyl groups are somewhat more powerful than the C = O in enhancing fluorescence.

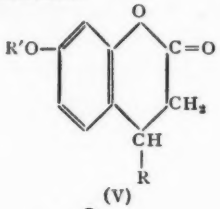
C. Effect of substitution in the 3 and 4 positions

Having observed and explained the remarkable influence of certain electron-attracting groups such as the carbonyl, cyano and phenyl in enhancing fluorescence, the question of the position of these groups comes in for consideration. When present in position 4 their effect on the resonance of the molecule should be very different from what has been described to take place in position 3. This has been tested in regard to two compounds, umbelliferone-4-carboxylic acid (VIII) and 4-phenylumbelliferone (IX). Comparison of their properties with those of the corresponding 3-substituted isomers shows the existence of large differences. The 4-substituted derivatives exhibit comparatively feeble fluorescence.

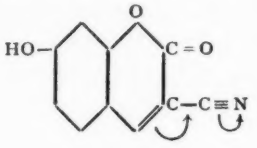
The reason for this marked difference between the two isomers seems to be as follows: When these groups are in position 3, conjugation (alternative single and double bonds) between them and the benzene ring is kept up and they reinforce the original resonance of umbelliferone. On the other hand when in position 4 they are not in conjugation with the benzene ring and may even work in antagonism to some extent as shown in VIII and IX.

D. Comparison of 3-carboxylic and 3-acetic acids

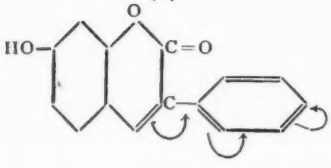
Another aspect of the influence of conjugation can be studied by comparing umbelliferone-3-carboxylic (IV, R = OH) and 3-acetic acids (X, R = OH). In the former, conjugation of the C = O group with the benzene ring exists whereas in the latter it is absent due to the intervention of a methylene group. Consequently, the 3-acetic acids should behave very similar to umbelliferone itself. This expectation is amply justified by the results presented in the table when observations relating to 7-hydroxycoumarin-3-acetic acid and its derivatives are compared with closely allied derivatives of 7-hydroxycoumarin-3-carboxylic acid. The presence of a methyl group in the 4-position in some of them is not expected to make any great difference.



(V)



(VI)



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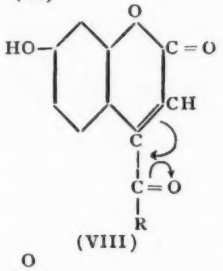
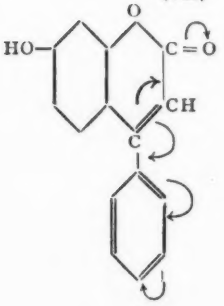
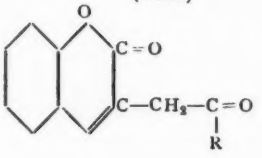


(VIII)



(IX)



(X)

E. Electron attracting groups in the benzene ring

When these groups are present in the benzene ring the normal movement of electrons towards the pyrone ring will be hampered and

consequently fluorescence should be diminished or lost. In Part I[1] the behaviour of a numbe- of substituted umbelliferones containing nitro, acetyl and formyl groups were recorded and the observations are according to the above expectations.

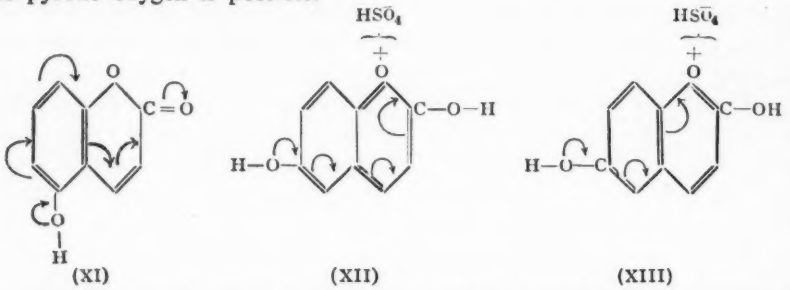
F. The effect of the position and number of hydroxyl groups on fluorescence

From the evidence already available it is clear that 7-hydroxy-coumarins emit fluorescence. Coumarin compounds containing only one phenolic hydroxyl group in position 5 have not so far been noticed to give fluorescence. The examples given in the Table confirm this observation. In general they give yellow solutions devoid of fluorescence. The behaviour of 6-hydroxy-coumarins is slightly different since they emit fluorescence in concentrated sulphuric acid solutions though not in others. 8-hydroxy-coumarin also does not give any fluorescence in spite of the fact that its solutions are not markedly coloured. The observation recorded by Bizzarri[3] that 8-hydroxy coumarin dissolves in alkali with a red colour and a blue fluorescence seems to be wrong. Obviously he was not dealing with the correct substance. Recently Dey and Kutti[4] have shown that his method of preparation employing catechol and malic acid is not satisfactory and they have obtained the correct compound by demethylating 8-methoxy coumarin. This substance does not exhibit any fluorescence. The same behaviour is noticed in the methyl ether and in 8-methoxy-coumarin-3-carboxylic acid. The lack of fluorescence in the last compound in spite of the favourable influence of the 3-carboxyl group is noteworthy. It may therefore be concluded that the position 7 is the most favourable one for a phenolic hydroxyl to enable the coumarin molecule to emit fluorescence.

In attempting an explanation of the above observations the behaviour of 7-hydroxy-coumarins is easily accounted for. The location of the hydroxyl group happens to be *para* to the position of branching of the unsaturated carbon system of the α-pyrone ring. Consequently resonance is easily favoured. A similar effect should be expected from the 5-hydroxyl (XI) which is in the ortho position. However in this case owing to the larger resonance possible, deeper absorption has occurred and fluorescence lost probably by the shift of the fluorescent band into the infra-red. It is interesting that 5-methoxy coumarins exhibit some fluorescence in neutral alcoholic solutions or in sulphuric acid. This seems to be due to a reduction of resonance and reduction of absorption so that flourescence band falls in the visible region. Even in the ethers, alkaline solutions do

not fluoresce. This may be attributed to the adverse effect of the hydroxyl ions on the C = O centre.

The 6 and 8-positions are meta and hence hydroxyls in these positions are not active. The feeble fluorescence of 6-hydroxy-coumarin in sulphuric acid may be attributed to the formation of oxonium salts of the following constitutions (XII, XIII) in which conjugation between the hydroxyl and the pyrone oxygen is possible.



(XI) (XII) (XIII)

With a view to study the influence of additional hydroxyl groups on the property of 7-hydroxy-coumarins a number of known compounds and new ones with the desired constitution have been prepared and examined very carefully. From the observations recorded in the Table it could be concluded that a second hydroxyl in position 6 diminishes the fluorescence. The inhibiting effect is greater when position 5 is involved and the emission is completely lost in 7 : 8-dihydroxy-compounds. It may be mentioned here that 5 : 7-dihydroxy coumarins have not been observed to emit fluorescence before. This may be due to the deep yellow solutions which they give in alkali. It is necessary to use very dilute solutions and employ very little alkali in order to observe correctly the feeble fluorescence that is emitted. A few compounds which are methyl ethers of 5 : 6 : 7-trihydroxy coumarin have been examined. They do not fluoresce thereby suggesting that the increase of the number of hydroxyls or methoxyls to more than two is not favourable to the development of fluorescence.

G. Effect of methylation

In the previous communications it has already been mentioned that the methylation of the hydroxyl groups brings about marked changes in fluorescence. The methyl ether of umbelliferone is indifferent to the addition of alkali whereas umbelliferone fluoresces brightly blue under these conditions. The ether exhibits a feeble fluorescence in concentrated sulphuric acid and the emission is more on the violet side. This has been attributed to the inability of the methoxyl to produce ions in alkali. Though

5-hydroxy-coumarin and its derivatives in which the hydroxyl group is free do not exhibit any fluorescence under any conditions, when the hydroxyl group is methylated or benzylated feeble fluorescence is exhibited in alcohol and sulphuric acid solutions. Similarly 6-methoxy coumarins fluoresce better than the corresponding hydroxy compounds. In these cases methylation is favourable to fluorescence. On the other hand methylation has no effect on 8-hydroxy-coumarin and both the hydroxy compound and its ether are non-fluorescent. There is thus some parallelism between the hydroxylic compounds and the methoxy derivatives in regard to the influence of position.

In Part I it was pointed out that C-methyl groups have a small influence though it is not very considerable. In a number of umbelliferone derivatives with a methyl group in the 8th position a tendency towards the production of green fluorescence in concentrated sulphuric acid is noticed whereas without it the emission is more towards blue and violet.

H. Fluorescence of some solids

Organic compounds which exhibit fluorescence in the solid state have been rare. Even certain dyes which emit strong fluorescence in solution do not show any in the solid state. This has been attributed to association and close packing of the molecules. During the course of the present investigation a number of compounds have been found to fluoresce in the crystalline condition. In general they give violet fluorescence. 7-acetoxy-3-phenyl-coumarin, 7-methoxy-3-phenyl coumarin, 7-methoxy-3-carbethoxy-coumarin, 7-methoxy-3-carboxy-coumarin and 7-methoxy-8-methyl-3-carbethoxy-coumarin give comparatively bright violet fluorescence. 7-methoxy-4-methyl-coumarin-3-ethylacetate, 7-methoxy-4-methyl-coumarin-3-acetic acid, 5-methoxy-4 : 7-dimethyl-coumarin-3-acetic acid, 5 : 7- dimethoxy-4-methyl-coumarin-3-ethylacetate and 5 : 7-dimethoxy-4-methyl coumarin-3-acetic acid give only weak violet fluorescence. It may be noted that the first four emit very strong fluorescence even in solution and the others yield solutions of comparatively feeble fluorescence. Most of the compounds are umbelliferone derivatives. Though many other similar substances may be expected to exhibit this property the occurrence of colour usually yellow makes the detection impossible. For the detection of solid flourescence it is necessary to purify the compounds thoroughly and it is especially necessary to remove impurities which may confer colour on the crystals. Though the first 4 compounds which are strongly fluorescent solids have been prepared before, this special property has not so far been detected mainly due to the fact that solid fluorescence is rather uncommon and fairly close observation is necessary to detect it. The best procedure is

to obtain the solid in the form of fine crystals and shake it in a clean test-tube so that it spreads over the sides to some extent.

Results of Observations

The following dihydroumbelliferone derivatives were examined. They did not exhibit any fluorescence under any condition. 7-hydroxy-3 : 4-dihydro-coumarin[5], 7-hydroxy-4-phenyl-3 : 4-dihydro-coumarin[6], 7-hydroxy-3 : 4-dihydro-coumarin-4-cyano-acetamide[7], 7-hydroxy-3 : 4-dihydro-coumarin–4–acetic acid[7], 7–methoxy–4–phenyl–3 : 4–dihydro–coumarin, 7–methoxy–3 : 4–dihydro–coumarin–4–cyano–acetamide[7], 7–methoxy–3 : 4–dihydro-coumarin-4-cyano-acetic acid[7], and 7-methoxy-3 : 4-dihydro-coumarin-4-acetic acid[7].

The following hydroxy and methoxy compounds did not exhibit any fluorescence under any condition : 5-hydroxy-4-methyl-coumarin[8], 5-hydroxy-4 : 7-dimethyl-coumarin[9], 5-hydroxy-4 : 7-dimethyl-coumarin-3-ethyl-acetate[10], 5-hydroxy-4 : 7-dimethyl-coumarin-3-acetic acid, 8-hydroxy-coumarin[4], 7 : 8-dihydroxy–4–methyl-coumarin[11], 7 : 8-dihydroxy–4–methyl-coumarin-3-ethyl-acetate[10], 7 : 8-dihydroxy-4-methyl-coumarin-3-acetic acid, 8-methoxy-coumarin[12], ethyl-8-methoxy-coumarin-3-carboxylate[13], 8-methoxy-coumarin–3–carboxylic acid[13], 5 : 7–dimethoxy–6–hydroxy–4–methyl-coumarin[14], 5 : 6 : 7-trimethoxy-4-methyl-coumarin[14], 7 : 8-dimethoxy-4-methyl-coumarin-3-ethyl acetate, 7 : 8-dimethoxy-4-methyl-coumarin-3-acetic acid, and 7 : 8-dimethoxy-4-methyl-coumarin.

Colour of visible fluorescence of Hydroxy and Methoxy compounds

Compound	In concentrated sulphuric acid	In alcohol	In dilute alkali
7-Hydroxy-3-acetyl coumarin	Pale blue	Violet blue; solution pale yellow	Solution yellow ; bright pale blue
7-Hydroxy-3-cyano coumarin	Deep yellow solution; blue fluorescence	Bright blue	Solution yellow ; bright blue fluorescence
7-Hydroxy-3-phenyl coumarin[15]	Deep blue fluorescence	Deep blue with violet tinge	Solution pale yellow ; exhibits bright blue fluorescence with a green tinge
7-Hydroxy-5-methyl-3-phenyl coumarin	Solution pale yellow; bright greenish blue	Bright-blue	Solution pale yellow ; exhibits bright greenish blue fluorescence
7-Hydroxy coumarin-4-carboxylic acid[16]	Feeble blue	Negligible (blue)	Solution pale yellow ; very feeble blue
7-Hydroxy-4-phenyl coumarin[11]	Blue	,,	Solution pale yellow ; very feeble green

Compound	In concentrated sulphuric acid	In alcohol	In dilute alkali
7-Hydroxy-4-methyl coumarin-3-ethyl acetate[17]	Violet blue	Pale blue	Solution colourless ; deep blue fluorescence
7-Hydroxy-4-methyl coumarin-3-acetic acid[17]	,,	,,	,,
6-Hydroxy coumarin[18]	Solution colourless; feeble blue fluorescence with a green tinge	Nil	Solution yellow ; no fluorescence
6-Hydroxy-4-methyl coumarin[16, 27]	,,	,,	,,
5 : 7-Dihydroxy-3-phenyl coumarin[19]	Solution yellow ; bluish green fluorescence	Weak blue	Solution yellow ; exhibits weak blue fluorescence
5 : 7-Dihydroxy-4-methyl coumarin-3-acetic acid	Solution pale yellow; feeble blue	Feeble blue	Solution yellow ; pale blue fluorescence stronger than in neutral alcohol
5 : 7-Dihydroxy-4-methyl coumarin-3-ethyl acetate	Feeble blue	,,	Solution yellow ; feeble blue fluorescence
5 : 7-Dihydroxy-4-methyl coumarin[20]	,,	,,	,,
6 : 7-Dihydroxy-4-methyl coumarin[21]	Violet blue	,,	Solution pale yellow ; feeble blue fluorescence
7-Hydroxy-8-methyl coumarin[22]	Bluish green	Very pale blue	Bright blue ; intensity increased
7-Hydroxy-8-methyl-3-acetyl coumarin	Solution yellow; pale green	Solution pale yellow; bright blue	Solution yellow ; strong blue
Ethyl-7-hydroxy-8-methyl coumarin-3-carboxylate	Solution colourless ; blue	Solution colourless ; bright blue	Solution very pale yellow ; strong blue
7-Hydroxy-8-methyl coumarin-3-carboxylic acid	,,	,,	,,
7-Hydroxy-8-methyl-4-phenyl coumarin	Colourless solution ; very feeble blue fluorescence	Nil	Nil
7-Acetoxy-3-phenyl coumarin[15]	Bright blue	Weak violet blue	Bright blue fluorescence
7-Methoxy-3-phenyl coumarin[23]	,,	Bluish violet	Bluish violet
7-Methoxy-5-methyl-3-phenyl coumarin	Solution yellow ; bright greenish blue	Violet	Violet

Compound	In concentrated sulphuric acid	In alcohol	In dilute alkali
7-Methoxy-4-methyl coumarin-3-ethyl acetate[17]	Bluish violet	Feeble violet	Feeble violet
7-Methoxy-4-methyl coumarin-3-acetic acid	,,	,,	,,
5-Methoxy-4-methyl coumarin[8]	Bluish green	Very weak blue	Very feeble violet
5-Methoxy-4 : 7-dimethyl coumarin[9]	,,	,,	,,
5-Methoxy-4 : 7-dimethyl coumarin-3-ethyl acetate	Very feeble blue	Weak blue	Feeble blue
5-Methoxy-4 : 7-dimethyl coumarin-3-acetic acid	,,	Feeble blue	,,
5-Benzyloxy-4 : 7-dimethyl coumarin	Feeble blue	,,	,,
6-Methoxy-4-methyl coumarin[27]	,,	,,	,,
5 : 7-Dimethoxy-3-phenyl coumarin	Bright green	Bright violet blue	Bright blue
5 : 7-Dimethoxy-4-methyl coumarin-3-ethyl acetate	Bluish green	Feeble bluish violet	Bluish violet
5 : 7-Dimethoxy-4-methyl coumarin-3-acetic acid	Bluish green	Feeble bluish viotet	Bluish violet
5 : 7-Dimethoxy-4-methyl coumarin[20]	,,	,,	,,
Ethyl-5 : 7-dimethoxy-6-hydroxy coumarin-3-carboxylate	Green	Pale yellow solution; no fluorescence	Pale yellow solution ; no fluorescence
7-Methoxy-8-methyl coumarin[22]	Bluish green	Very pale violet	Very pale blue
8-methyl-7-methoxy-3-acetyl coumarin	Solution yellow ; green fluorescence	Violet	Solution yellow ; blue fluorescence on dilution with water
Ethyl-8-methyl-7-methoxy coumarin-3-carboxylate[22]	Green	,,	Fluorescence lost ; addition of acid or large dilution restores fluorescence
8-Methyl-7-methoxy coumarin-3-carboxylic acid[22]	Bright green	,,	Flourescence lost ; restored on dilution or addition of acid

Note.—In the case of compounds which do not dissolve in dilute aqueous alkali, alcoholic solutions were employed and a few drops of aqueous alkali added before observing fluorescence.

Experimental

Preparation of the necessary compounds

7-Hydroxy-3-acetyl-coumarin.—This was originally prepared by Weiss and Merksammer[24] using resorcinol and ethoxymethylene-ethyl-aceto-acetate. It is more easily prepared by condensing β-resorcylic aldehyde (1·0 g.) with ethyl aceto-acetate (1·5 g.) employing piperidine as the condensing agent. The product is recrystallised from alcohol when it is obtained in the form of light yellow rectangular crystals melting at 236-37° ; yield 1·3 g. (Found : C, 68·5 ; H, 4·1 ; $C_{11}H_8O_4$ requires C, 68·6 ; H, 3·9%.)

7-Hydroxy-3-cyano-coumarin.—A mixture of cyanoacetic ester (3·0 g.) and β-resorcylic aldehyde (2·0 g.) was treated with 4 drops of piperidine and left overnight. It was then digested with cold water and filtered ; the solid residue was washed with ether and dried. The crude product thus obtained was recrystallised from absolute alcohol when yellow rectangular plates melting at 262° were obtained. (Found : N, 7·7 ; $C_{10}H_5O_3N$ requires N, 7·5%.) It is easily soluble in acetone and sparingly in ether and chloroform.

7-Hydroxy-5-methyl-3-phenyl-coumarin.—It was previously prepared by Badhwar *et al.*[25] by condensing orcinol with benzoyloxymethylenephenyl-aceto-nitrile and subsequently hydrolysing the resulting compound. The following procedure has now been found to be more covenient : Orcylic aldehyde (1·5 g.), dry sodium phenyl acetate (3 g.) and acetic anhydride (20 c.c.) were thoroughly mixed in a 100 c.c. conical flask and heated in an oil-bath at 170-80° for 4 hours. The product was then poured into water and let stand for several hours. The separated crystals of 7-acetoxy-5-methyl-3-phenyl-coumarin were filtered, washed with much water and then with a little ether. The substance was then deacetylated by dissolving in alcohol, adding 20 c.c. of 10% caustic soda and heating on a boiling water-bath for 15 minutes. 7-hydroxy-5-methyl-3-phenyl-coumarin obtained on acidification, crystallised in long light yellow needles from alcohol and melted at 233°.

7-Hydroxy-8-methyl-3-acetyl-coumarin.—This was prepared by the condensation of 3-methylresorcylaldehyde (0·5 g.) with ethyl aceto-acetate (0·8 g.) using piperidine as the condensing agent. When crystallised from alcohol it came out as long light yellow rectangular plates which melted at 256--57°. Yield 0·8 g. (Found : C, 61·0 ; H, 5·1 ; $C_{12}H_{10}O_4$, H_2O requires C, 61·0 ; H, 5·1%.)

Ethyl-7-hydroxy-8-methyl-c o u m a r i n-3-carboxylate.—3-methylresorcyl-aldehyde (0·5 g.) was condensed with diethyl malonate (0·6 g.) using

piperidine as the condensing agent. The product crystallised from alcohol as long pale yellow rectangular plates and melted at 250-51°. Yield 0·7 g. (Found : C, 63·2 ; H, 5·2 ; $C_{13}H_{12}O_5$ requires C, 62·9 ; H, 4·8%.)

7-*Hydroxy*-8-*methyl-coumarin*-3-*carboxylic acid* resulted from the hydrolysis of the above ester using 20% methyl alcoholic potash in the cold. It crystallised from alcohol as yellow rectangular plates and melted at 277-78°.

7-*Hydroxy*-8-*methyl*-4-*phenyl-coumarin.*—Concentrated sulphuric acid (1·2 g.) was added to an intimate mixture of 2-methyl resorcinol (0·5 g.) and ethyl benzoylacetate (0·5 g.) and the solution was kept overnight. It was then poured into ice water next morning. The solid product was filtered, washed with ether and recrystallised from alcohol when it came out in lustrous rhombohedral tablets and melted at 279-80°. Yield 0·9 g. (Found : C, 76·4 ; H, 4·8 ; $C_{16}H_{12}O_3$ requires C, 76·2 ; H, 4·8%.)

5-*Hydroxy*-4 : 7-*dimethyl-coumarin*-3-*acetic acid.*—The ester (1 g.) prepared according to the method of Chakravarti[10] was dissolved in 10% sodium hydroxide solution (15 c.c.) and kept in a water-bath at 60-70° for about 15 minutes. The solution was then cooled and acidified with dilute hydrochloric acid. The acid separated out gradually as a colourless solid. On recrystallisation from alcohol, it came out in the form of shining plates and melted at 271°. (Found : C, 62·5 ; H, 4·7 ; $C_{13}H_{12}O_4$ requires C, 62·9; H, 4·8%.) It is soluble in acetone and insoluble in ether, benzene and chloroform.

5 : 7-*Dihydroxy*-4-*methyl-coumarin*-3-*ethyl-acetate.*—To a mixture of phloroglucinol (4 g.) and ethyl acetosuccinate (6 g.), 10 c.c. of concentrated sulphuric acid was added in small quantities with much shaking. It was kept for one hour and poured into water. The separated solid was filtered, washed with water and crystallised from alcohol when it came out in clusters of colourless needles melting at 240°. (Found : C, 60·7 ; H, 4·8 ; $C_{14}H_{14}O_6$ requires C, 60·4 ; H, 5·0%.)

5 : 7-*Dihydroxy*-4-*methyl-coumarin*-3-*acetic acid.*—It was obtained by hydrolysing the above ester with alkali as in the previous case. It formed colourless needles with rounded edges melting at 264°, when recrystallised from alcohol. (Found : C, 57·5 ; H, 4·2 ; $C_{12}H_{10}O_6$ requires C, 57·6 ; H, 4·0%.) It is soluble in acetone and insoluble in ether and chloroform.

7 : 8-*Dihydroxy*-4-*methyl-coumarin*-3-*acetic acid.*—7 : 8-dihydroxy-4-methyl-coumarin-3-ethyl acetate (1·0 g.) prepared according to the method of Chakravarti[10] was hydrolysed to the acid by the usual method using sodium hydroxide as described previously. The acid on crystallisation from aqueous alcohol came out in colourless rectangular plates melting

at 277°. (Found: C, 57·6; H, 3·9; $C_{12}H_{10}O_6$ requires C, 57·6 ; H, 4·0%.) The substance is soluble in acetone and chloroform and sparingly soluble in ether.

7-methoxy-3-acetyl-8-methyl-coumarin.—2-hydroxy-4-methoxy-3-methyl-benzaldehyde[22] (0·5 g.) was mixed with ethyl aceto-acetate (0.8 g.) and piperidine (10-15 drops) was added slowly while cooling in ice. It was allowed to stand overnight. The solid was treated with excess of dilute hydrochloric acid ; after filtration the residue was recrystallised from alcohol when it came out in long colourless rectangular plates, melting at 191-92°. (Found : C, 66·9 ; H, 5·1 ; $C_{13}H_{12}O_4$ requires C, 67·2 ; H, 5·2%.)

5: *7-Dimethoxy-6-hydroxy-3-carbethoxy-c o u m a r i n.*—3 : 5-dimethoxy-quinolaldehyde (1·0 g.) prepared according to the method of Späth and Jezmanowska-Siekiewiczowa[25] was intimately mixed with ethyl malonate (1·5 g.) and piperidine (2 drops) was added. The mixture was slightly warmed on a water-bath until a clear solution resulted and it was left overnight. Next morning, it was poured into water and the solid obtained was recrystallised from alcohol, when it came out in long yellow needles melting at 190°. (Found : C, 57·5 ; H, 4·5 ; $C_{14}H_{14}O_7$ requires C, 57·2; H, 4·8%.) It is easily soluble in ether, acetone and chloroform.

5: *7-Dimethoxy-6-hydroxy-coumarin-3-carboxylic acid.*—This was obtained from the above ester by hydrolysis using 10% sodium hydroxide solution. It recrystallised in colourless rectangular prisms from dilute alcohol and melted at 252°. (Found: C, 54·3, H, 4·0 ; $C_{12}H_{10}O_7$ requires C, 54·1 ; H, 3·8%.) It is easily soluble in acetone and chloroform and moderately in ether.

The following are methoxy compounds obtained by the methylation of the appropriate hydroxy compounds, by means of excess of methyl iodide and anhydrous potassium carbonate in dry acetone solution. The general procedure will be clear from the following example.

7-Methoxy-4-p h e n y l-3 : 4-dihydro-coumarin.—7-hydroxy-4-phenyl-3 : 4-dihydro-coumarin (1 g.) prepared according to the method of Liebermann and Hartmann[6] from resorcinol and cinnamic acid, was dissolved in dry acetone (20 c.c.). The solution was treated with anhydrous potassium carbonate (3·0 g.) and methyl iodide (4 g.) and the mixture kept gently boiling for about 6 hours. The solution was then filtered, the solvent removed by evaporation and the residue crystallised from alcohol. The methyl ether came out as colourless long rectangular plates and melted at 43-44°. (Found: C, 72·8; H, 6·0 ; $C_{16}H_{14}O_3$, $\frac{1}{2}H_2O$ requires C, 73·0; H, 5·7%.)

7-Methoxy-5-methyl-3-phenyl-coumarin.—This was obtained by the methylation of 7-hydroxy-5-methyl-3-phenyl-coumarin. On recrystallisation from alcohol, it came out as stout golden yellow rectangular prisms and melted at 155°. (Found: C, 76·9; H, 5·5; $C_{17}H_{14}O_3$ requires C, 76·6; H, 5·3%.) It is moderately soluble in acetone and sparingly in ether and chloroform.

7-Methoxy-4-methyl-coumarin-3-ethyl-acetate is easily prepared by the above method from the corresponding 7-hydroxy compound.[17] It was originally prepared by a different method by Banerjee.[17]

5-Methoxy-4:7-dimethyl-coumarin-3-ethyl-acetate.—This resulted from the methylation of the corresponding 5-hydroxy compound which was prepared according to the procedure of Chakravarti[10]. The methyl ether when crystallised from alcohol came out in long colourless needles melting at 117°. (Found: C, 66·3 ; H, 6.1 ; $C_{16}H_{18}O_5$ requires C, 66·2 ; H, 6·2%.) The substance is soluble in acetone, chloroform and ether.

5-Methoxy-4:7-dimethyl-coumarin-3-acetic acid.—The above ester was dissolved in aqueous alcoholic potash and heated just to boiling. It was cooled and the acid obtained on acidification was recrystallised from alcohol when it came out in long colourless needles melting at 225°. (Found: C, 64·0; H, 5·6; $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·3%.) It is easily soluble in acetone and chloroform but with difficulty in ether.

5: 7-Dimethoxy-3-phenyl-coumarin was prepared by the methylation of 5: 7-dihydroxy-3-phenyl-coumarin[19]. On crystallisation from alcohol it came out in colourless rectangular plates melting at 179-80°. (Found: C, 68·4; H, 5·3; $C_{17}H_{14}O_4$, H_2O requires C, 68·0; H, 5·3%.) It is soluble in acetone and chloroform and less so in ether.

5: 7-Dimethoxy-4-methyl-coumarin-3-ethyl-acetate.—This was prepared from the corresponding dihydroxy compound described in this paper. It cyrstallised from aqueous alcohol as colourless shining plates, and melted at 134°. (Found: C, 62·4; H, 5·7; $C_{16}H_{18}O_6$ requires C, 62·8; H, 5·9%.) It is soluble in acetone and ether and moderately so in chloroform.

By the hydrolysis of the above ester using aqueous alcoholic potash the corresponding acid, *5: 7-dimethoxy-4-methyl-coumarin-3-acetic acid* was obtained. It crystallised from alcohol as colourless rectangular plates rounded at the edges melting at 218-20°. (Found: C, 60·6, H, 5·0; $C_{14}H_{14}O_6$ requires C, 60·4 ; H, 5·0%.) It is sparingly soluble in chloroform and ether.

7 : 8-Dimethoxy-4-methyl-coumarin-3-ethyl acetate was obtained from the corresponding dihydroxy compound[19]. The substance crystallised

in long colourless needles from dilute alcohol and melted at 87°. (Found : C, 63·2 ; H, 5·7 ; $C_{16}H_{18}O_6$ requires C, 62·8 ; H, 5·9%.) It is soluble in ether, acetone and chloroform.

The corresponding 3-*acetic acid* was prepared by the hydrolysis of the above ester using aqueous alcoholic potash. It crystallised from alcohol as colourless rectangular prisms melting at 194°. (Found : C, 60·5 ; H, 5·4 ; $C_{14}H_{14}O_6$ requires C, 60·4 ; H, 11·5%.) It is easily soluble in acetone and chloroform but moderately in ether.

5-*Benzyloxy*-4 : 7-*dimethyl-coumarin.*—5-Hydroxy-4 : 7-dimethyl-coumarin (1 g.) was dissolved in acetone (25 c.c.) and to the solution was added benzyl chloride (1·5 g.) and anhydrous potassium carbonate (3 g.). The mixture was refluxed on a water-bath for about 12 hours. The solvent was then distilled off, and water was added to the residue and kept overnight. Crystals of 5-benzyloxy-4 : 7-dimethyl-coumarin and a little unchanged benzyl chloride gradually separated out. The substance was filtered and washed with a little ether to remove the benzyl chloride. On recrystallisation from dilute alcohol, stout colourless prisms melting at 150° were obtained. (Found: C, 77·4 ; H, 6·0 ; $C_{18}H_{16}O_3$ requires C, 77·1; H, 5·7%.) It is easily soluble in acetone and moderately in ether.

Observation of fluorescence.—There is no difficulty in observing fairly strong fluorescence but when it is weak, it may be missed unless careful observation is made. Bright sunlight helps in such cases and if a concentrated beam of light could be obtained using a lens the emission of fluorescence becomes clearer. As the most satisfactory method of observing fluorescence using diffused day light, the following has been employed in this investigation. A round flat-bottomed flask filled with water and commonly used as a wash-bottle is kept on a table with a dark surface in the path of diffused day light from a door or window. When the test solution contained in a test-tube is placed in the patch of light thus focussed, weak fluorescences are readily visible. With a view to eliminate discrepancies, comparison is made with the particular solvent contained in the same test-tube. Solutions having colour were examined after progressive dilution in order to see if fluorescence appeared at any stage.

Summary

From the data presented in the paper, the following points have been established: (1) Dihydro-umbelliferone and its derivatives, in which the pyrone double bond does not exist, do not give any fluorescence. (2) Similar to the carbonyl group cyano and phenyl groups enhance fluorescence emission markedly when present in the 3 position of umbelliferone. (3) No

such effect is noticed when these groups occupy position 4. (4) A similar lack of influence is noticed in umbelliferone-3-acetic acid and its derivatives in which a methylene group breaks the conjugation. (5) Amongst monohydroxy coumarins, the presence of the hydroxy group in position 7 is most effective ; in position 6, a feeble effect exists ; in positions 5 and 8 no fluorescence is noticed. (6) Amongst dihydroxy-coumarins 6 : 7, 5 : 7, 8 : 7, represent a decreasing series, the last giving no fluorescence. Derivatives of higher polyhydroxy-coumarins do not exhibit fluorescence. (7) Effect of methylation of the hydroxyl groups introduce marked changes in the capacity of the compounds to fluoresce and the colour of the fluorescence. 5-Methoxy-coumarin emits a feeble fluorescence whereas 8-methoxy compounds do not. (8) A few compounds exhibit fluorescence in the solid state. The above observations are explained from the effect of the structural features on the resonance of the molecule.

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ON A THEOREM OF J. L. WALSH CONCERNING THE MODULI OF ZEROS OF POLYNOMIALS

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Let $P(z) = a_0 + a_1 z + \cdots + a_n z^n$ $(a_0 a_n \neq 0)$ be a polynomial. There are many known results concerning the regions in which the zeros of $P(z)$ are located. Some of these results are obtained from a consideration of the moduli alone of the co-efficients $a_0, a_1, \cdots a_n$. For instance if the modulus of z be so small that $|a_0|$ exceeds the sum of the moduli of all the other terms then obviously $P(z) \neq 0$. Thus if R_0 is the sole positive root of the equation

$$|a_0| - |a_1| z - |a_2| z^2 - \cdots - |a_n| z^n = 0$$

then $P(z) \neq 0$ inside the circle $|z| < R_0$. The proof is easy since

$$|a_0| > |a_1 z| + |a_2 z^2| + \cdots + |a_n z^n| \tag{1}$$

whenever $|z| < R_0$. It is also easy to see that the inequality (1) holds for no value of z for which $|z| \geqslant R_0$. Similar remarks apply if $|z|$ be so large that $|a_n z^n|$ exceeds the sum of the moduli of all the other terms of $P(z)$. Thus, if R_n is the sole positive root of the equation

$$|a_0| + |a_1| z + \cdots + |a_{n-1}| z^{n-1} - |a_n| z^n$$

then $P(z) \neq 0$ when $|z| > R_n$. For, if $|z| > R_n$ then

$$|a_n z^n| > \sum_{r=0}^{n-1} |a_r z^r|. \tag{2}$$

The inequality (2) does not hold if $|z| \leqslant R_n$. These results are due to Cauchy. By applying similar arguments to any other term $a_k z^k$ $(0 < k < n)$ similar results can be obtained. Consider the equation

$$|a| + |a_1| z + \cdots + |a_{k-1}| z^{k-1} - |a_k| z^k + |a_{k+1}| z^{k+1} + \cdots + |a_n| z^n = 0.$$

From Descarte's *rule of signs* it is seen that this equation has either no positive root or just two positive roots ; if the equation has two positive roots R_k and R_k', and if they be distinct,* say, $R_k < R_k'$ then $|a_k z^k|$ exceeds the sum of the moduli of the other terms if (and only if) $|z|$ lies between

* If $P(z) = z^2 + 5z + 6$ then $R_0 = 1$, $R_1 = 2$, $R_1' = 3$, $R_2 = 6$.

R_k and R_k'. These considerations led A. E. Pellet† to the following very useful theorem:

If the equation

$$\sum_{r=0}^{k-1} |a_r| z^r - |a_k| z^k + \sum_{r=k+1}^{n} |a_r| z^r = 0 \quad (0 < k < n)$$

has two distinct positive roots R_k and R_k' $(R_k < R_k')$ then the polynomial $P(z) = a_0 + a_1 z + \cdots + a_n z^n$ has no zeros in the annulus $R_k < |z| < R_k'$, and has precisely k zeros in the circle $|z| \leqslant R_k$.

To prove that there are precisely k zeros of $P(z)$ in the circle $|z| \leqslant R_k$ Pellet utilizes the theorem of Rouché. In his paper‡ entitled *On Pellet's theorem concerning the roots of a polynomial*, J. L. Walsh gave a more direct proof of Pellet's theorem and also established a sort of converse of the theorem, there being no valid direct converse of the theorem. Walsh considers the set G of polynomials

$$a_0\epsilon_0 + a_1\epsilon_1 z + \cdots a_n\epsilon_n z^n \tag{3}$$

where $\epsilon_0, \epsilon_1, \cdots \epsilon_n$ vary independently and assume all values of modulus 1. Let S be the set of zeros of all polynomials that belong to G. It is obvious that if a number α belongs to S then the same is true of every number whose modulus is equal to $|\alpha|$. From what has been said already it is clear that α cannot be a member of S if any of the following inequalities hold:

$$|\alpha| < R_0, \quad |\alpha| > R_n, \quad R_k < |\alpha| < R_k', \tag{4}$$

where $k = 1, 2, \cdots, n-1$, and k is such that R_k and R_k' exist. Suppose now that α satisfies none of the inequalities (4). The following question arises: Is such a number α necessarily a member of S? Walsh's theorem states that the answer is in the affirmative. In a recent paper§ A. Ostrowski pointed out that Walsh's proof of this important result is not complete, and gave a proof of his own. Ostrowski's proof of Walsh's theorem utilizes the theorem of Rouché. It is desirable that such a result as Walsh's theorem should be proved without the use of Rouché's theorem, and by entirely elementary reasoning. The object of this note is to provide such a proof. The proof given in this note is a modification of Ostrowski's proof.

THEOREM 1. *Let G be the set of polynomials*

$$a_0\epsilon_0 + a_1\epsilon_1 z + \cdots + a_n\epsilon_n z^n \tag{5}$$

† A. E. Pellet, "Sur un mode de séparation des racines des équations et la formule de Lagrange," *Bulletin des Sciences Mathématiques* (2), 1881, **5**, 393–95.

‡ *Annals of Mathematics*, 1924, **26**, 59–64.

§ Alexander Ostrowski, "On a theorem by J. L. Walsh concerning the moduli of roots of algebraic equations," *Bulletin of the American Math. Soc.*, 1941, **47**, 742–46.

where $a_0, a_1, \cdots a_n$ are fixed and $\epsilon_0, \epsilon_1, \cdots \epsilon_n$ assume independently all values of modulus 1, *and S be the set of zeros of polynomials that belong to G. If α is not a member of S then there is a number m $(0 \leqslant m \leqslant n)$ such that $|a_m\alpha^m|$ exceeds the sum of the moduli of the other terms, i.e.,*

$$|a_m\alpha^m| > -|a_m\alpha^m| + \sum_{r=0}^{n} |a_r\alpha^r|.$$

Remark.—From what has been stated already it is obvious that the conclusion of Theorem 1 implies that $|\alpha|$ satisfies one of the inequalities (4). Hence if $|\alpha|$ satisfies none of the inequalities (4) then α is necessarily a member of *S*.

Theorem 1 is plainly a corollary of

THEOREM 2. *Let T denote the set of values of the expression*

$$f(\eta_0, \eta_1, \cdots \eta_n) = C_0\eta_0 + C_1\eta_1 + \cdots + C_n\eta_n$$

where $C_0, C_1, \cdots C_n$ are fixed and $\eta_0, \eta_1, \cdots \eta_n$ assume independently all values of modulus 1. *If the number zero does not belong to the set T then there is an integer m $(0 \leqslant m \leqslant n)$ such that*

$$|C_m| > -|C_m| + \sum_{r=0}^{n} |C_r|.$$

We can suppose, without loss of generality, that $C_0, C_1, \cdots C_n$ are real and positive, and that

$$C_0 \geqslant C_1 \geqslant \cdots \geqslant C_n. \tag{6}$$

If the conclusion of the lemma be not true then plainly there exists an integer t $(0 \leqslant t \leqslant n-2)$ such that

$$\sum_{r=0}^{t} C_r \leqslant \sum_{r=t+1}^{n} C_r, \quad \sum_{r=0}^{t+1} C_r > \sum_{r=t+2}^{n} C_r. \tag{7}$$

Let

$$\phi(\epsilon) = \left(\epsilon C_{t+1} + \sum_{r=0}^{t} C_r\right) \Big/ \sum_{r=t+2}^{n} C_r$$

From (6) and (7) we see that

$$0 \leqslant \phi(-1) \leqslant 1 < \phi(1).$$

Now, since $\phi(\epsilon)$ varies continuously as ϵ varies (continuously) along the periphery of the unit circle it follows that for a suitable value of ϵ,

$$1 = |\epsilon| = |\phi(\epsilon)|.$$

If $\eta = -\phi(\epsilon)$, and $\eta_r = 1$ or ϵ or η according as r is less than or equal to or greater than $t+1$ then

$$f(\eta_0, \eta_1, \cdots \eta_n) = \sum_{r=0}^{t} C_r + \epsilon C_{t+1} + \sum_{r=t+2}^{n} \eta C_r = 0,$$

a contradiction that proves the theorem.

Suppose that for all small positive values of δ neither $x-\delta$ nor $y+\delta$ $(0<x<y)$ belongs to S. Then it is easy to deduce that each polynomial of G has the same number of zeros in the closed annulus $x \leqslant |z| \leqslant y$, for, if we vary continuously the factors ϵ_r in the representation (5), the zeros of (5) vary continuously and their number within the annulus concerned remains the same since none of them is able to get across the boundary of the annulus. From this observation it follows that if

$$R_0, R_1, R_1', R_2, R_2', \cdots R_{n-1}, R'_{n-1}, R_n \; [R_t < R_t'; t=1, 2, \cdots n-1]$$

all exist then each of the following annuli

$$R_0 \leqslant |z| \leqslant R_1, \quad R_t' \leqslant |z| \leqslant R_{t+1} \; (t=1, 2, \cdots n-1)$$

contains at least one zero of each member of G. [For one thing $R_1, R_2, \cdots R_n$ are members of S.] It can be shown by very elementary reasoning that the annuli are all distinct, and since they are n in number it follows that each annulus contains precisely one zero of each member of G. As the zero in each annulus is able to migrate from one circle to the other circle bounding the annulus (for, $R_0, R_1, R_1', \cdots R_{n-1}, R'_{n-1}, R_n$ are all members of S) it follows that every member α that belongs to an annulus is also a member of S. This constitutes another proof of Walsh's theorem in the case in which $R_0, R_1, R_1', \cdots R_n$ all exist, but we need some such result as Theorem 2 of this note to dispose of the case in which some or all of the numbers $R_1, R_1', \cdots R'_{n-1}$ do not exist.

Summary

Alexander Ostrowski recently gave a proof of a result which is a conditioned converse of a theorem of A. E. Pellet. The theorem proved by Ostrowski is due to J. L. Walsh, but it was pointed out by Ostrowski that Walsh's proof of his theorem was incomplete. Ostrowski's proof utilizes the theorem of Rouché whereas the result proved concerns the moduli of zeros of polynomials. This note contains a proof of Walsh's result by elementary reasoning which is more appropriate to the subject. The result proved is that *if*

$$P(z) = a_0 + a_1 z + \cdots + a_n z^n,$$

and α is such that for $z=\alpha$ the modulus of no term of $P(z)$ exceeds the sum of the moduli of all the other terms of $P(z)$ then α is a root of some equation

$$b_0 + b_1 z + \cdots + b_n z^n = 0$$

where $|a_r| = |b_r|$, $(r = 0, 1, 2, \cdots, n)$.

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